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MODERN CHEMICAL PROCESSES

A Series of Articles Describing
Chemical Manufacturing Plants

*by the Editors of
Industrial and Engineering Chemistry
in conjunction with the technical staffs
of the cooperating organizations*

VOLUME II

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FOREWORD

The editors of *Industrial and Engineering Chemistry* are very pleased to cooperate with the Reinhold Publishing Corporation in the publication of Volume II of "Modern Chemical Processes," a compilation of twenty-four plant process articles, published once a month in *Industrial and Engineering Chemistry* under the general title of "Staff-Industry Collaborative Reports."

The series was inaugurated in the February, 1948, issue of *Industrial and Engineering Chemistry* and the first twenty-three articles appeared as Volume I of "Modern Chemical Processes," published in the fall of 1950. It was the intention of Reinhold Publishing Corporation at that time to issue a volume every two years if Volume I was well received. Its favorable reception by industrial chemists and chemical engineers indicates that this plan will probably be carried out.

I believe a brief description of the philosophy behind the publication of the "Staff-Industry Collaborative Reports" is in order.

Industrial and Engineering Chemistry does not suffer from a dearth of articles. Indeed, over the years somewhere between thirty to forty per cent of the manuscripts offered for publication are rejected, not all, however, because they do not meet the high editorial standards of the journal. If the editors believe that a particular manuscript more correctly belongs in some other journal it is promptly released. The primary objective of the editors of *Industrial and Engineering Chemistry* is the most effective presentation of the scientific and technical literature in such a way as to provide maximum and most effective service to the user.

There are areas of chemical technology, however, which in the past have not been adequately covered by papers presented at professional society meetings or offered directly to the chemical journals.

Recognizing these gaps in the literature the editors of *Industrial and Engineering Chemistry* have initiated a number of special features, such as the "Staff-Industry Collaborative Reports" and "Pilot Plants," to mention just two of many such services.

Each plant process article is written by an associate editor in collaboration with company engineers and operating officials. The editors have insisted that each article must be of solid content in chemical, manufacturing, and engineering knowledge and techniques and those which have not met these standards have been discarded.

The editors are particularly happy to point out that many new company names appear in this second volume of "Staff-Industry Collaborative Reports." Again thanks is due to all company officials who have permitted their plants or processes to be described in a very thorough and comprehensive manner. Thanks are due also to the engineers and operating officials who have cooperated as co-authors to the associate editors who have served as senior authors.

If I, as editor of *I&EC*, may be permitted to inject a personal note, I wish to express my appreciation of the efforts of D. O. Myatt, managing editor, in directing the series, and to acknowledge publicly the contributions of the associate editors and other staff members of *Industrial and Engineering Chemistry* to the continuing success of the series. The modern Chemical Processes Series, a new volume of which is issued every other year, has earned a very special place in the chemical engineering literature. The "Staff-Industry Collaborative Reports" provide the most modern and up-to-the minute production and engineering data published anywhere. Publication of these articles biennially in book form provides a ready reference for the industrial chemist, the chemical engineer, the technically trained chemical executive, the teacher, and the advanced student, the value of which will increase as additional volumes appear.

WALTER J. MURPHY, *Editor*
Industrial and Engineering Chemistry

Washington, D. C.
March 3, 1952

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CHEMICALS FROM FATS



McCook, Ill., Plant of Armour and Company

Hydrogen plant, left; hydrogenation building and fat-splitting tower, center; still battery, right

RICHARD L. KENYON

Associate Editor

in collaboration with

D. V. STINGLEY AND H. P. YOUNG

Armour and Company, Chicago, Ill.

FATS and fatty compounds are extremely widespread in their occurrence and are vital factors in human, animal, and plant existence. Various lipids, including glyceride esters or fats, glycerophosphoric acid esters or phosphatides, and related fatty compounds occur in almost every type of plant and animal cell and often represent a large part of the total constituents of specialized organs, such as seeds, nuts, tubers, livers, intermuscular connective tissue, and other tissues. However, according to Markley (17), probably less than a thousand fats from all sources have been examined, even superficially, and the known fats and oils of economic or industrial significance probably do not exceed a few hundred.

The history of the use of fats and fatty acids is apparently older than the written history of mankind. Mixtures of palmitic acid and tripalmitin and of stearic acid and tristearin have been found in Egyptian tombs believed to predate the first dynasty (17), and it is reported that olive oil was used as a lubricant for moving large stones, as well as for axle grease, as early as 1400 B.C. (14). The ancients lighted their quarters with "rush light," a sort of candle made by soaking the pith of certain reeds in animal fats (16). "Tallow dip" candles, made by dipping a string into beef fat, were the next developments in this type of lighting and candles made of a mixture of tallow and beeswax were known to the Romans. The decomposition of the fat during burning to produce fumes of acrolein, which irritated the eyes, may have led to a search for improvement which produced the hydrolysis of fats. Scheele, in 1779, made glycerol by heating olive oil with litharge, but it was Chevreul who is generally credited with the discovery in 1815 that tallow could be treated chemically to yield glycerol and hard, high-melting, waxy fatty acids. This led to the making of improved candles as well as to

an interest in the chemistry of fats and the acids derived from them. Poutet, in 1819, converted oleic acid to elaidic acid by treatment with oxides of nitrogen. Gusserow, in 1828, differentiated oleic and other unsaturated acids from palmitic and stearic acids on the basis of the difference in solubilities of the lead salts.

Thereafter, however, the interest seems to have been light and little progress was made in the fundamental chemistry of fats and oils until after the beginning of the twentieth century, according to Markley (17), who says "and this despite the fact that during the nineteenth century the most brilliant and far-reaching discoveries were being made in many fields of organic chemistry." It was notable that even as late as 1924 the chemistry of fats was a section of science given little attention. At about that date there was a strong renaissance which led, through studies by a number of workers, to a much more detailed knowledge of the constitution of fats, to the chemistry of fatty acids, and subsequently to the use of fatty acids as raw materials for the production of other types of useful chemical compounds.

CHEMICAL NATURE OF FATS AND FATTY ACIDS

Fatty acids occur in nature almost exclusively as esters, usually glycerides, seldom in the free state. Although it has been reported that free acids have been found in the fats of ripe seeds, it is considered questionable as to whether they existed in that form naturally or were converted during their extraction for examination (26). The naturally occurring glycerides are dealt with extensively in a number of authoritative texts (2, 8-11, 13, 15).

The naturally occurring glyceride mixtures generally contain at least five, and frequently more, different fatty acids and only small percentages of simple triglycerides, such as triolein. In

nature the mixtures are usually highly heterogeneous (26). The particular acids found are influenced by environment. Marine fats usually contain highly unsaturated, high molecular weight (C_{18} to C_{24}) acids associated with only small amounts of saturated acids. The fats from land animals contain large amounts of the C_{16} and C_{18} saturated and unsaturated acids. Those of vegetable origin contain substantial amounts of one or more closely related acids characteristic of the particular source: coconut oil contains large amounts of lauric acid and closely related acids; castor oil is high in ricinoleic acid; and tung oil high in eleostearic acid.

Palmitic acid is the most abundant and widely distributed of the naturally occurring saturated fatty acids. It is found in almost every fatty substance investigated so far (26). Stearic acid is an important constituent of all animal life and many vegetable fats and waxes. The most important unsaturated acids are oleic, linoleic, and linolenic. Acids containing more than eighteen carbons usually are present only as minor constituents of animal and vegetable fats, although sometimes in appreciable quantities in marine fats and in plant and insect waxes. Acids containing less than sixteen carbons are frequently found in vegetable oils, but, with the exception of milk fats, are not major components of animal fats. It has been observed that when one member of a series of the saturated fatty acids is present in a large amount, the next higher and lower homologs are found to some extent. It is now generally accepted that the naturally occurring acids contain a normal, unbranched chain of carbon atoms, and only those of an even number of carbons exist in natural fats. Exceptions are found in dolphin and porpoise oil and the oil from valerian roots, all of which contain isovaleric acid.

CHEMISTRY OF FAT AND FATTY ACID PROCESSING

Fatty acids may be obtained from the fats, or glycerides, either by the old familiar soap-kettle procedure of saponification with sodium hydroxide followed by acidulation or by other splitting methods. Most of the commercial fatty acids made in the United States are prepared by one of four processes. These are discussed and compared in detail by Marsel and Allen (18): The oldest is the high pressure autoclave batch process (29, 30). The other batch method is the Twitchell process (2) in which water and a catalyst are used. Of the continuous processes, one is concurrent (7) and the other is countercurrent. The last mentioned is found in two modifications, one of these is known as the Procter and Gamble process (19), the other is the Colgate-Emery process (3, 12). The latter is employed in the Armour plant. The products of this splitting are fatty acids and glycerol:

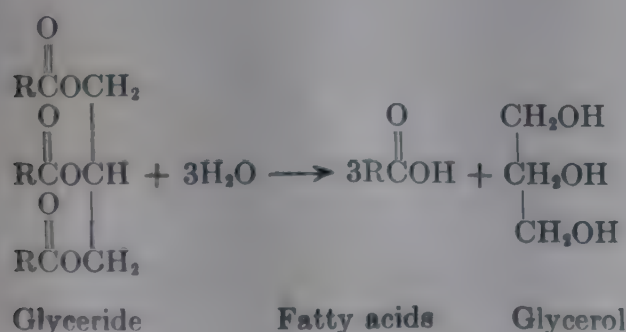


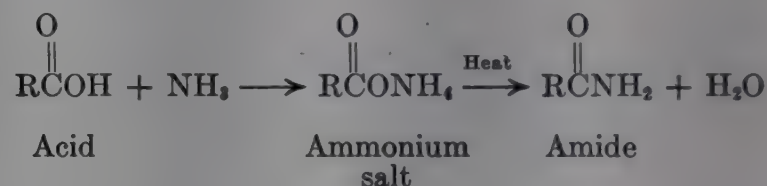
TABLE I. FATTY ACIDS MOST COMMONLY FOUND IN NATURE

Common Name	Geneva Nomenclature	Chemical Formula	Molecular Weight	Melting Point, °C.
Saturated acids				
Acetic	n-Ethanoic	CH_3COOH	60.05	16.6
Butyric	Butanoic	$\text{C}_3\text{H}_7\text{COOH}$	88.10	-7.9
Caproic	Hexanoic	$\text{C}_5\text{H}_{11}\text{COOH}$	116.16	-2.0
Caprylic	Octanoic	$\text{C}_7\text{H}_{15}\text{COOH}$	144.21	16.5
Capric	Decanoic	$\text{C}_9\text{H}_{19}\text{COOH}$	172.26	31.3
Lauric	Dodecanoic	$\text{C}_{11}\text{H}_{23}\text{COOH}$	200.31	43.6
Myristic	Tetradecanoic	$\text{C}_{13}\text{H}_{27}\text{COOH}$	228.37	53.8
Palmitic	Hexadecanoic	$\text{C}_{15}\text{H}_{31}\text{COOH}$	256.42	62.8
Stearic	Octadecanoic	$\text{C}_{17}\text{H}_{35}\text{COOH}$	284.47	69.9
Arachidic	Eicosanoic	$\text{C}_{19}\text{H}_{39}\text{COOH}$	312.52	75.3
Unsaturated acids				
Oleic	cis-9-Octadecenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	282.46	13.4
Elaidic	trans-9-Octadecenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	282.46	51.5
Linoleic	9,12-Octadecadienoic	$\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	280.44	-6.5
Linolenic	9,12,15-Octadecatrienoic	$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	278.42	-12.8
Eleostearic	9,11,13-Octadecatrienoic	$\text{CH}_3(\text{CH}_2)_2\text{CH}:\text{CHCH}:\text{CHCH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	278.42	49.0

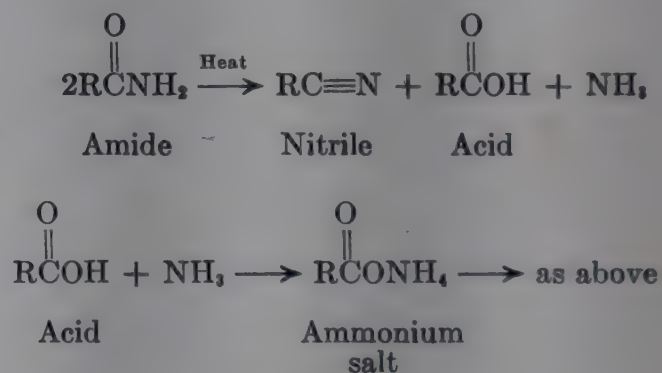
The commercially more important fatty acids are described in Table I. The fatty acids are difficult to separate. Saturated acids can be separated from unsaturated by crystallization (6), and acids of different chain length are separated by fractional distillation (21).

The fatty acids undergo many of the typical reactions of carboxylic acids, the ease of reaction usually decreasing with the length of the carbon chain. Those reactions used in the manufacture of the products with which this paper is concerned are shown here.

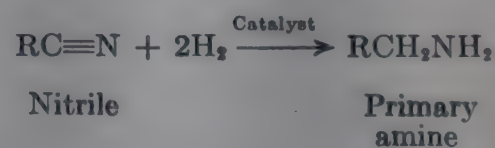
Acids react with ammonia to form ammonium salts, which on heating lose one mole of water to yield amides:



By heating amides to high temperatures, there are formed nitriles, along with fatty acid and ammonia. In the presence of excess ammonia, the fatty acid is again converted into an ammonium salt and the process is repeated until eventually the conversion to nitrile is quantitative:

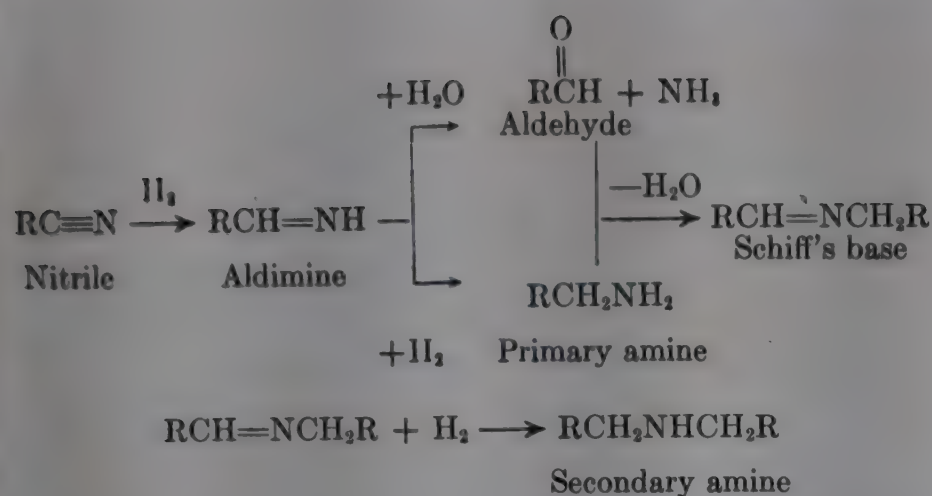


The addition of two moles of hydrogen to a nitrile, with the aid of a catalyst, yields a primary amine:

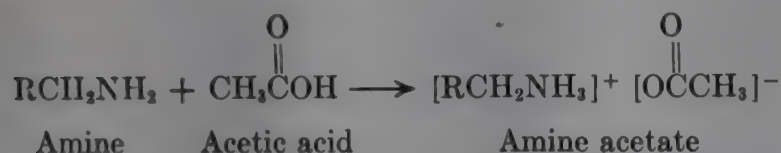


The formation of a secondary amine is more complex. Apparently the nitrile is converted to an aldimine by partial hydrogenation. The aldimine then reacts in part with water to yield an aldehyde and ammonia and in part with hydrogen to yield a primary amine. The aldehyde and amine then can form a Schiff's base, which is reduced to a secondary amine:

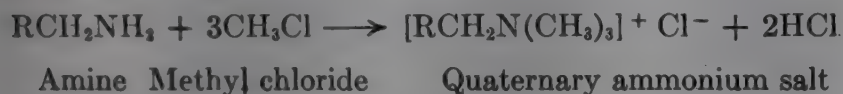




Amines, being basic, can form salts with acids—for example, amine acetates through the reaction with acetic acid:



Amines can also form salts, called quaternary ammonium salts, through the reaction with 3 moles of an alkyl halide, methyl chloride, for example:



In the Armour plant, all of these reactions are carried out, beginning with fatty materials. The starting materials are, for the most part, tallow, greases (which include lard and other packing house fats), fish oils, and coconut oils.

DEVELOPMENTS BY ARMOUR

Armour and Company began to process fatty acids near the turn of the century with the distillation of low grade materials for soapmaking. The operation was a part of the soap plant and was developed in the interest of utilization of waste materials through their improvement for use as soap oils. The entire production of this work was used by the company in the manufacture of soap.

World War I provided a strong impetus to the better utilization of fats, and both equipment and methods were improved. Shortly thereafter Armour had six cast-iron stills with copper condensers and receivers in operation for the distillation of fatty acids. With these facilities production was increased to the extent that in addition to supplying the company's needs, small quantities of acids were sold, going to manufacturers of lubricating greases and to small scale soapmakers.

During the 1920's, the complexion of the fatty acid business became much less favorable than it had been. Market differentials changed and many producers went out of business. Armour met this condition with a decision to separate the acids and improve their value. Research in this direction bore fruit with the building of the first fractional distillation unit for the separation of fatty acids, based on the patent of Potts and McKee (23); this still went into operation in 1933. Specially fractionated acids, made to specification, were offered to the trade. The venture was successful and a second fractionating still was installed in 1941. These installations were built at the Armour plant at 1355 West 31st Street, Chicago, Ill.

In the meantime, research and development in derivatives of fatty acids had produced other needs for plant expansion. About 1930 there had been set up at the laboratories of Armour and

Company, in the Chicago stockyards, a research group whose task was to improve the value of fats, then at a particularly low point. Success was achieved in the preparation of useful nitrogen-containing derivatives of fatty acids (25) and a small pilot plant was built in 1935. The unit was enlarged in 1937 and commercial quantities were produced.

The first carload of high molecular weight primary amines, in drums, was shipped June 21, 1940, and a little more than two years later tank car shipments had begun. The first commercial scale plant for the production of high molecular weight nitriles and primary amines derived from fatty acids went into operation in September 1942. This plant employed processes for nitrile and amine manufacture which had been developed in the Armour laboratories (22, 27, 28, 31).

The demand for fractionated fatty acids and for the nitrogen-containing derivatives made it clear that facilities at the plant on 31st Street were not ample. The result has been the building of a new plant at McCook, Ill., which started operations in September 1949 and is designed for the processing of more than 100,000,000 pounds of raw fats and oils per year. In addition to manufacturing the products mentioned, the plant will also manufacture high purity fatty acids, particularly oleic, stearic, palmitic, and linoleic acid, by fractional crystallization in solvent.

MCCOOK, ILL., PLANT OF ARMOUR AND COMPANY

Raw Materials Receiving. Fats are received in railroad tank cars which are weighed on track scales before entering the unloading shed. They are then unloaded by means of steam-driven reciprocating pumps, having extra-large valves, connected to the bottom valve of the tank car by means of a flexible metal hose, and the contents are pumped to the storage tanks beside the unloading shed. The empty tank car is weighed as it leaves the shed, which has a concrete floor with sumps beneath the car positions to receive any material which may be spilled accidentally. These sumps drain to a catch basin which can be pumped out to the storage tanks. Low voltage lights (25 volts) are suspended from the ceiling on reels, for use in cleaning out the empty tank cars. Sodium hydroxide solution, ammonia, acetic acid, and sulfuric acid, also received in tank cars, are unloaded at separate stations nearby.

Storage tanks of carbon steel, each with a capacity of 1,000,000 pounds, are located beside the unloading house to receive all the incoming products.

Fat Refining. Fats may go directly to hydrogenation as received or may be refined in preparation. Usually animal fats and fish oils go through the refining process. Vegetable oils, as coconut and palm oil, are not usually refined. Because of the low volume of fats refined and the variable charge stock used in this plant, the older batch process is used rather than the centrifugal process.

In refining, the fat is stirred in an open, conical-bottomed kettle with dilute alkali, of about 20° Bé. strength, which removes all acids. The resulting foots settle to the bottom; the oil is pumped off through a swinging suction line; the foots are drained out through a bottom valve to an acidulation tank; and the acid product is added to unrefined materials which will go directly to splitting.

The refined oil is pumped to a bleach tank, heated to drive off moisture, stirred with bleaching clay, and passed through a vertical plate filter. It is then ready for hydrogenation as a refined oil.

Fat Hydrogenation. At the side of the hydrogenation building there are five hydrogenation vessels, each of 10,000-pound charge capacity, fitted with shrouded turbine agitators, and internal heating and cooling coils. Two of these vessels, which are used for fats and fatty acids, are clad with Type 316 stainless steel. The other three, one for fats and oils and two for the reduction of nitriles to amines, are of carbon steel. In order to minimize the explosion hazard no hydrogen lines enter the hydrogenation



Fat Refining and Splitting Area

Tops of sweet water evaporators (left); acidulation kettle for treatment of foots (center); and half-crude bleaching kettle (right)

building. This is made possible by the exterior location of the vessels. Catalyst preparation equipment, filters, pumps, and controls are located inside the building.

Raw hydrogen, containing carbon monoxide and carbon dioxide, is prepared by catalytic reaction of natural gas and steam in a standard plant unit (4E). The carbon monoxide in the raw hydrogen is converted to carbon dioxide by the water gas shift reaction in three stages. After cooling in each stage, the carbon dioxide is removed by scrubbing the gas with monoethanolamine. Because of the nitrogen content of the natural gas, the finished hydrogen gas contains 2 to 3% nitrogen, but this is no disadvantage in the utilization process. The capacity of the plant is 300,000 standard cubic feet per day.

Fats prepared for hydrogenation are pumped from their respective storage tanks to the hydrogenation vessels, where reduced nickel formate catalyst is added. The hydrogenation is carried out at pressures in the neighborhood of 150 pounds per square inch and temperatures of 175° to 200° C., using about 0.25% by weight catalyst (calculated as nickel). After completion of the treatment, the charge is blown directly to stainless steel horizontal plate filter presses. Nitrogen pressure forces the oil through filter paper, removing the catalyst, thence to a small tank where it is held while chemical control tests are carried out. Some catalyst is re-used, some new material being added with each charge. After approval by the control laboratory, the oil is

pumped to a large tank in the storage area, where it awaits transfer to the splitter for the preparation of fatty acids.

Fat Splitting. The Colgate-Emery process (3) is used for the splitting of fats to glycerol and fatty acids. Pressures of about 650 pounds per square inch gage and temperatures of about 245° C. are used in the process. Temperatures, pressures, and flow rates are regulated by pneumatic controllers. The column is a 3 × 67 foot steel unit, lined with low carbon Type 316, stainless steel spot-welded to the tower shell (1E), which is heavily insulated with magnesia block. Both fats and water are charged into it by means of three vertical triplex pumps. One pump feeds oil, one water, and one is interchangeable as a relief for either of the others. The pumps are served by small tanks, providing about one day's run, which receive the fats from the receiving storage tanks or from the refining unit.

Fat is charged into the bottom of the column through a sparge ring, which breaks it into small droplets, and rises through the hot "sweet water" into the fat phase where it is heated by direct contact with steam sparged into the lower sector of the column at about 245° C. Hydrolysis of the glycerides takes place as the material continues to pass upwards. Heat is maintained in this section of the column by a center steam sparge. Water is charged into the top of the column, by another vertical pump of the same type, through a sparge ring and is heated by direct contact with the fatty acids. Additional heat, to 245° C., is supplied by steam.

The finely dispersed water falls through the fat-fatty acid mixture, effecting hydrolysis, and the sweet water solution of glycerol (10 to 12%) collects in the bottom of the column where it is discharged by an automatic interface controller.

The sweet water passes to a double-effect evaporator and is evaporated to "half-crude" (45% glycerol). The half-crude is treated with bleaching clay by heating and stirring in a kettle and is filtered through a plate-and-frame filter. Evaporation is continued to obtain saponification crude glycerin (90% glycerol). The glycerin is shipped to another plant for refining to the desired grades.

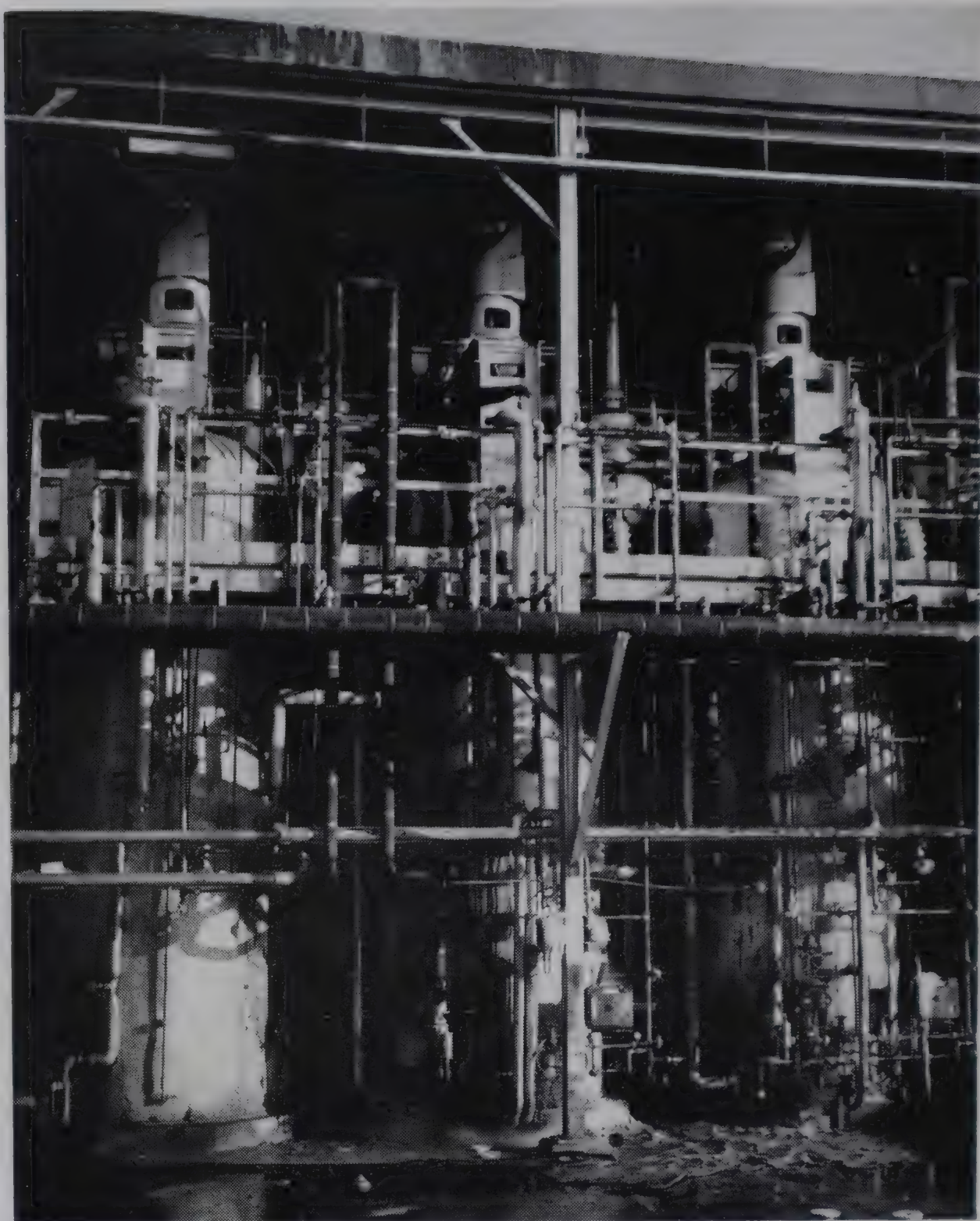
The fatty acids from the splitter pass directly to a crude fatty acid storage tank to await distillation.

PROCESSING OF FATTY ACIDS

Fatty acids from the splitter storage tank are distilled according to the specifications of the products desired. A triple column still system (20), developed as an improvement over the system mentioned previously, is used; all three stills are bubble-plate units of Type 316 stainless steel, designed for very low pressure drop. Each is fitted with a shell-and-tube condenser which is connected, through a catch pot, to a barometric condenser and to a two-stage steam-jet ejector. Thermocompressor boosters are located in the lines of the second and third between the condensers and the catch pot. Each still has a Dowtherm re-boiler near its base. The system has a capacity for handling 3500 pounds of fatty acids feed per hour. The stills are operated at constant pressures and a maximum base temperature of 250° C. The first column, operating at a pressure measuring 40 mm. at the column head, yields a distillate, part of which is returned as reflux. The take-off is a very small portion which consists of acids in the lower boiling range. It usually contains unsaponifiables and is known as the "odor cut." Bottoms pass through a flow controller, which regulates the take-off rate to maintain a set level in the tower to column two. This column operates at a pressure of about 5 mm. at the top of the column. An intermediate cut is taken off and the bottoms run down to the third column, directly below, operating at a pressure of 5 mm., where cut three is taken. The bottoms from this still are pumped to the stearine pitch tank. Condensed product from the catch pot is drained back to the first still.

The distilled fatty acids are pumped to storage tanks. From there liquid and low melting acids may be pumped to tank cars for shipment or to a drum filler, where they are put into 55-gallon drums for less-than-carload-lot shipment. These materials are also the starting products for the manufacture of amides, by ammoniation, at another plant.

The final step in the preparation of high melting acids is accomplished by pumping the molten acid to a smaller steam-heated tank from which the liquid is pumped to rotary drum flakers. The molten slurry is fed at a constant rate through a trough



Three of Five Hydrogenation Vessels Located beside Hydrogenation Building

from which the overflow returns to the feed tank. A chromium-plated rotating drum, chilled by an internal spray of water, dips into the trough, picking up a thin film of the acid which solidifies. After a 270° turn, the solid film is removed by a scraper, falls into a conveyer hopper, and is carried to a bag filler which collects it in 50-pound paper bags.

Nitrile Preparation. Fatty acids, for the production of the desired nitriles, are centrifugally pumped to a Type 316 stainless steel shell-and-tube reflux condenser with a floating head at the top of the ammoniation reaction tower. This tower is a bubble-plate column of Type 316 stainless steel, having an internal U-tube reboiler. The feed is preheated as it passes through the condenser tubes and enters the tower at one of the lower plates. The reflux stream from the shell returns to the top plate of the tower. Combination with ammonia takes place here and in addition nitrile formation occurs. Bottoms from the reaction tower run to a small bubble-plate stripping tower, called the pitch tower, where all fatty acids and ammoniated products are stripped out by the incoming ammonia and carried back into the tower. The residue from the pitch tower is pumped to a storage tank to be marketed as nitrile pitch. The product leaving the reaction tower through the reflux condenser in vapor form consists of nitrile, fatty acid, ammonia, and water. The mixture passes through a Dowtherm-heated shell-and-tube superheater and enters a converter containing a fixed bed of aluminum



Amine Acetate Production Unit

Amines and acetic acid are fed to mixing tank (*left foreground*); product is pumped directly to drums before it has cooled to the solidification point

oxide catalyst. The converter is a shell-and-tube unit with catalyst packed in the tubes and Dowtherm circulating in the shell to provide heat. Here the conversion to nitriles is completed. The product, in vapor phase, containing mostly nitriles, less than 0.5% unconverted fatty acids, ammonia, and water, passes out the bottom of the converter to a small bubble-plate stripping column. From this stripper, the crude nitriles are withdrawn as bottom product and are either pumped to storage tanks or fed, by gravity, directly to a vacuum fractionating still system very similar to the type described for fatty acid fractionation. Water is removed from the stripper as a side stream, for disposal, and ammonia, containing less than 3% water, passes through the condenser to a rotary compressor and thence to the ammonia feed superheater and back to the ammonia system. Make-up ammonia is added ahead of the superheater. A continuous bleed on the compressor discharge passes through a small water-spray absorber, which scrubs out the ammonia and returns it as an aqueous solution to the stripper; any noncondensable gases go to the atmosphere.

Amine Preparation. The catalyst used for the conversion of nitriles to amines is Raney nickel. It is prepared by stirring Raney aluminum-nickel alloy with 25° Bé. aqueous sodium hydroxide until the aluminum is completely dissolved. The liquor is decanted and the catalyst washed thoroughly with water. The first two washings are added to the decanted caustic liquor,

which is evaporated in a steam concentrator to yield marketable sodium aluminate. The catalyst is stored under water until used. It is re-used during the process of reduction of the nitrile.

Primary amines are prepared at about 150° C., under 200 pounds per square inch hydrogen pressure in the presence of the catalyst. Yields of about 85% of primary amine result; the balance is secondary and tertiary amines. In the reduction of nitriles aimed at the production of secondary amines, higher temperatures and a different catalyst are used.

Amines are distilled from a pot still through a single column having 2 or 3 plates; the still serves merely to remove the small amounts of secondary and tertiary amines present. After distillation, the amines are pumped to storage tanks. They may be utilized in any of three ways: conversion to amine acetates; conversion to quaternary amine salts; or marketed as primary or secondary amines.

Amine Acetates. Amine acetates are not stored in tanks, as they are solids which tend to dehydrate on heating to the melting point after formation and solidification, yielding substitute amides. The acetates are prepared on order for immediate shipment and are run directly into shipping drums from which they are dissolved by the user. Amines are pumped from storage tanks into a feed tank from which they are pumped by a proportioning pump into a mixing tank containing water-cooler coils. Acetic

acid is fed into the tank at a metered rate by another proportioning pump (5E) coordinated with the amine feed to yield the acetate directly in a continuous process. The mixture is stirred and cooled to remove the heat of reaction. The acetate, still liquid at about 75° C., is taken off directly to a drum filler, which automatically fills the drums with 400 pounds of the product.

Quaternary ammonium salts are prepared by treatment of amines with methyl chloride at another plant.

Crystallization of Fatty Acids. The unit for the crystallization of fatty acids is the last section of the plant to be completed and is not yet in operation.

AUXILIARY INSTALLATIONS

Storage and Transfer. In a plant with flow lines as flexible as those found here, storage is a major problem, as many products must be held for use according to a great variety of specifications. It follows that the transfer of materials is also important.

Fats, nitriles, and amines are stored in carbon steel tanks and the pipe lines for the transfer of these materials are the same. Fatty acids for processing are stored in Type 347 stainless steel-clad steel tanks and carried in pipes of the same material. Finished product fatty acids are stored in aluminum tanks.

All piping, including that for utilities, except service water to cooling towers and for fire service, is overhead. All product lines are steam traced and are insulated with magnesia-asbestos pipe covering and wrapped with waterproof paper.

As many of the finished products are either solids or semisolids when cooled, a special type heating system is applied to the finished product storage tanks. To avoid excessive localized heating which may cause decomposition of the products, all heating pipes, which carry steam, are outside the tanks. These pipes are in the form of series of U-tubes which lie in shallow rectangular grooves in the concrete base on which the tank stands. The base is closed in with asbestos paper and tar coating for insulation, but can be opened readily. Thus repairs on the tank-heating system are relatively simple. The entire bottom of the tank is heated evenly and the heat transmitted through the contents of the tank by means of liquid convection currents. The heating tubes receive steam at 15 pounds per square inch from the exhaust steam mains. Finished product storage tanks are enclosed in a sheet iron building.

To prevent oxidation, all finished products are stored under an atmosphere of nitrogen. The nitrogen atmosphere is produced in an automatic system (3E) by the balanced combustion of natural gas with air. Carbon dioxide is scrubbed out with monoethanolamine.

Centrifugal pumps are used for the most part; those which handle fatty acid materials are of Durimet 20 stainless steel.

Horizontal, valve plate, piston pumps are used for unloading raw materials. Those used for fatty acids are of Type 316 stainless steel. Vertical, triplex, valve plate pumps are used for charging the splitter.

Water, Steam, Heat, and Power. Water for the entire plant is drawn from the city supply to a covered reservoir of 500,000-

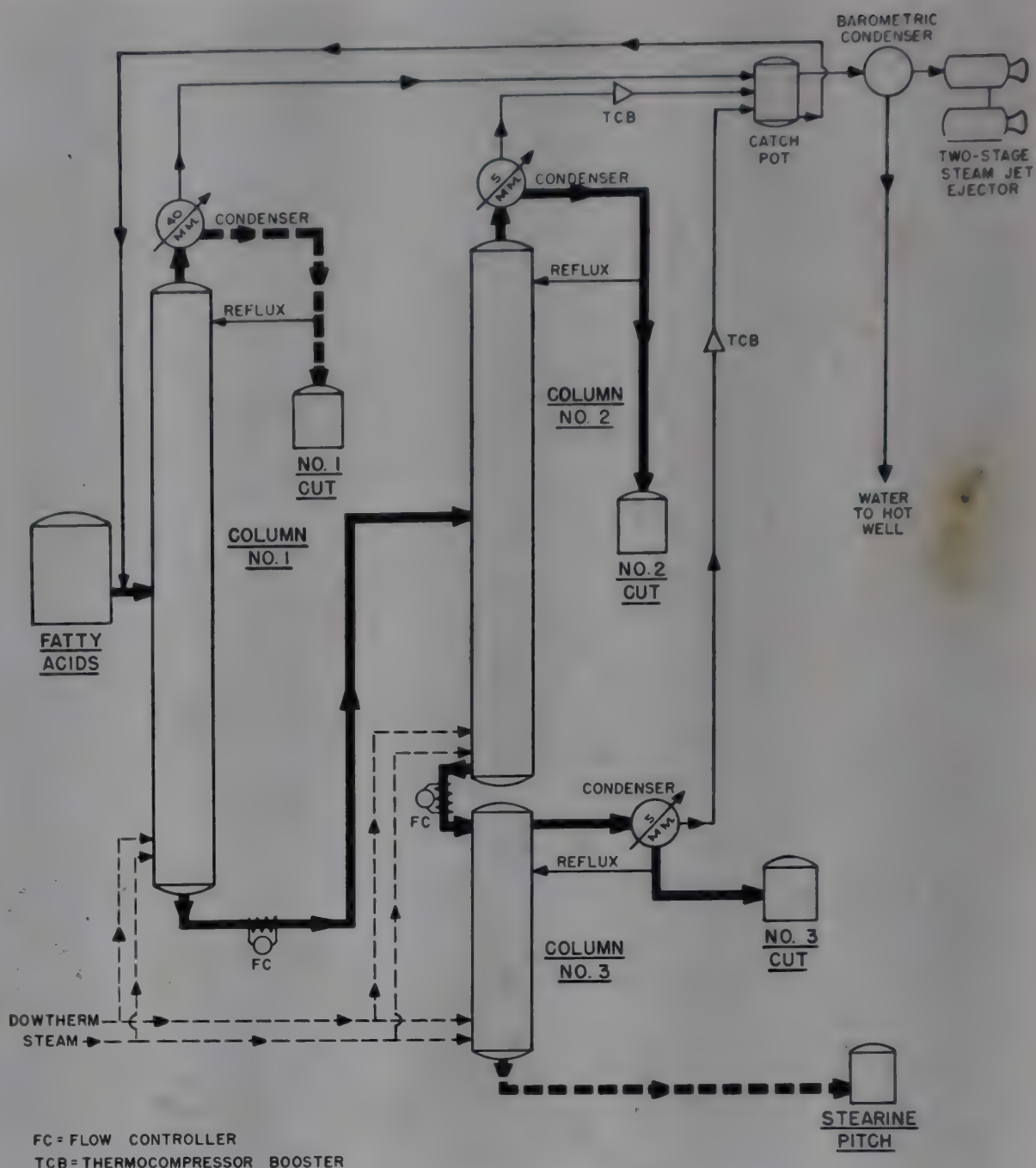


Figure 3. Fatty Acid Still System

gallon capacity. This reservoir can be drawn down only to the half-full level for plant use, the remainder being reserved exclusively for the fire-fighting system.

Two spray-cascade type cooling towers are maintained. One of these is a clean-water tower from which water circulates in a closed system and furnishes the condensers, except those in the still area, and heat exchangers. The oily-water cooling tower handles the water from the barometric condensers in the glycerin, nitrile, and fatty acid processing systems. This water is pumped from the cooling towers to the barometric condensers and flows by gravity back to the skimmer basins, where it is clarified for recirculation.

Two completely closed systems, cooled by water from the clean-water cooling tower, are maintained. The water in these is exposed to the air only in expansion tanks, and make-up is steam condensate. The systems furnish water for the condensers in the fatty acid and nitrile distillation systems, respectively.

Two skimmer basins are maintained. One receives process sewage from catch basins, floor washings, and spillage, and the other receives oily water from the barometric condensers. Mechanical skimmers collect the oily layer from the top of the water for grease recovery. In addition to the process sewage system, there is a separate storm and drainage system.

Steam is furnished to the entire plant by boilers at one location. All except high pressure steam is furnished by two 40,000-pound-per-hour, coal-fired boilers of standard design. High pressure steam for the splitter is furnished at 725 pounds per square inch gage by a 4000-pound-per-hour gas-fired boiler. Heat for the plant buildings is furnished by exhaust steam, at 20 pounds of pressure, from the plant system.



Hydrogen Production Plant

The Dowtherm system consists of three vapor generators of 4,500,000-B.t.u.-per-hour capacity each, which may be either gas- or oil-fired; switching is possible without interruption. The vapor generators are fully automatic and can be controlled from the still room. The three generators are so organized that any two can carry the full plant load. In normal operation all three are used to avoid overloading. They are connected by a manifold so that any generator can serve any of the three systems (fatty acid distillation, nitrile conversion, or nitrile distillation). However, each of these systems has its own vapor header and condensate header.

In addition to this system for heating with Dowtherm vapor, there is a liquid Dowtherm system for heating the nitrile converter. This system takes its heat through a heat exchanger from the Dowtherm vapor system.

Electric power is taken directly from the public service lines.

Instrumentation. Rotameter-type flow controllers were chosen on the basis of experience. They have been found preferable in handling fatty acids and their derivatives as they are self-cleaning, have no pressure tap in which hard fat can solidify, and the transmission is electric directly from the instrument. Electronic and galvanometer multiple-point strip chart temperature recorders, multiple-point instantaneous indicators, and bulb-type temperature controllers are used in the plant.

Pressure gages are standard, with diaphragm gage protectors on product lines. Float-type level controllers, exterior to the tower, having a torque arm transmission to the diaphragm have been used almost exclusively. Absolute pressure recorders are employed at the tops of the stills with mercury manometers at the bottoms.

Air for pneumatic instruments and diaphragm valves throughout the entire plant is supplied through a separate system at a pressure of 60 pounds per square inch and a dew point of $+60^{\circ}\text{F}$.

An interesting feature of the plant is the calibration of nearly all temperature recording and control instruments on the centigrade scale.

TABLE II. LABORATORY STUDIES ON CORROSION EFFECTS OF TALL OIL

Alloy	Corrosion, Inches per Year			
	285° C.	300° C.	315° C.	330° C.
Type 316 stainless (2.2% Mo)	0.004	0.004	0.072	0.05
Type 317 stainless (3.34% Mo)	0.005	0.008	0.021	...
Inconel	0.01	0.01	0.015	0.011
Type 302 stainless	0.175	0.497	0.804	...
Hastelloy C	0.004	0.005	0.004	...

MATERIALS OF CONSTRUCTION AND CORROSION

Experience in earlier plants with fatty acid stills lined with Ka2S stainless steel was not satisfactory because of excessive corrosion. Tests with Ka2SMo indicated that it was superior, with the result that this material was adopted as standard for all fatty acid equipment. In the new plant Type 316 stainless steel, which is a variant of the earlier Ka2SMo, is used throughout where there is contact with fatty acids (24).

There is an exception to the rule in the heater tubes, where the temperature rises above 300°C . It was found that under these conditions the corrosion of Type 316 increases substantially as the



Flaker for Solid Fatty Acids

Warm, liquid acid is pumped from tank (left) into flaker trough; chromium plated roll, cooled by internal water spray picks up fatty acid film which solidifies, is removed by doctor knife, and conveyed to bagging unit

temperature rises, whereas Inconel maintains its resistance. Results of some studies using tall oil, one of the most corrosive handled in the plant, are shown in Table II.

Another effect which was not understood well in earlier work was the effect of welding on the resistance of materials. It has been observed that where linings or vessels are not heat-treated after welding, the susceptibility to corrosion is particularly strong about 0.5 inch from the line of the weld. This defect is overcome by heat treatment after fabrication of the vessel.

The specification of low carbon content (less than 0.03% maximum) gives a steel which is not subject to carbide precipitation from the effects of welding. The use of such a steel makes possible the fabrication of corrosion-resistant linings without heat treatment.

A considerable amount has been said in the literature on the subject of the resistance of materials to corrosion by fatty acids (4, 5).

CHEMICAL CONTROL

Uniformity of products is ensured through the establishment of specifications and by checking samples of product in process, as well as final product samples. Plant operators have been taught to run process control samples in the plant. The final product samples are taken by a laboratory technician and appropriate samples run by analytical chemists in the laboratory. General

tests consist of the determination of significant and well known values, such as iodine value, saponification or acid value, titration and color reading. Ultraviolet spectrophotometric methods are used to determine quantitatively the presence of polyunsaturated fatty acids. For control purposes, the primary amine content of the fatty amines is adequately indicated by direct titration.

Emphasis is placed on simplicity, speed, and frequency of testing, but elaborate testing is performed where it is called for by the nature of the product. Variety in the types and grades of finished products is great. Control tests are tailored to fit the specific requirements for each. Thus chemical control for the products of this plant is complex. Shipment of the product is not proved until laboratory tests have been completed on the final sample.

PRODUCTS AND THEIR USES

Fatty Acids. The commercial fatty acids which are produced are caprylic, capric, lauric, myristic, palmitic, and stearic. The principal unsaturated acids are oleic and linoleic. The products sold, under the Armour trade-mark Neo-Fats, are fractionally distilled fatty acids with percentages of the major components ranging up to 95%. Others of these commercial fatty acids are mixtures of two similar homologs, such as oleic and linoleic. This is particularly true of the unsaturated products. Some are

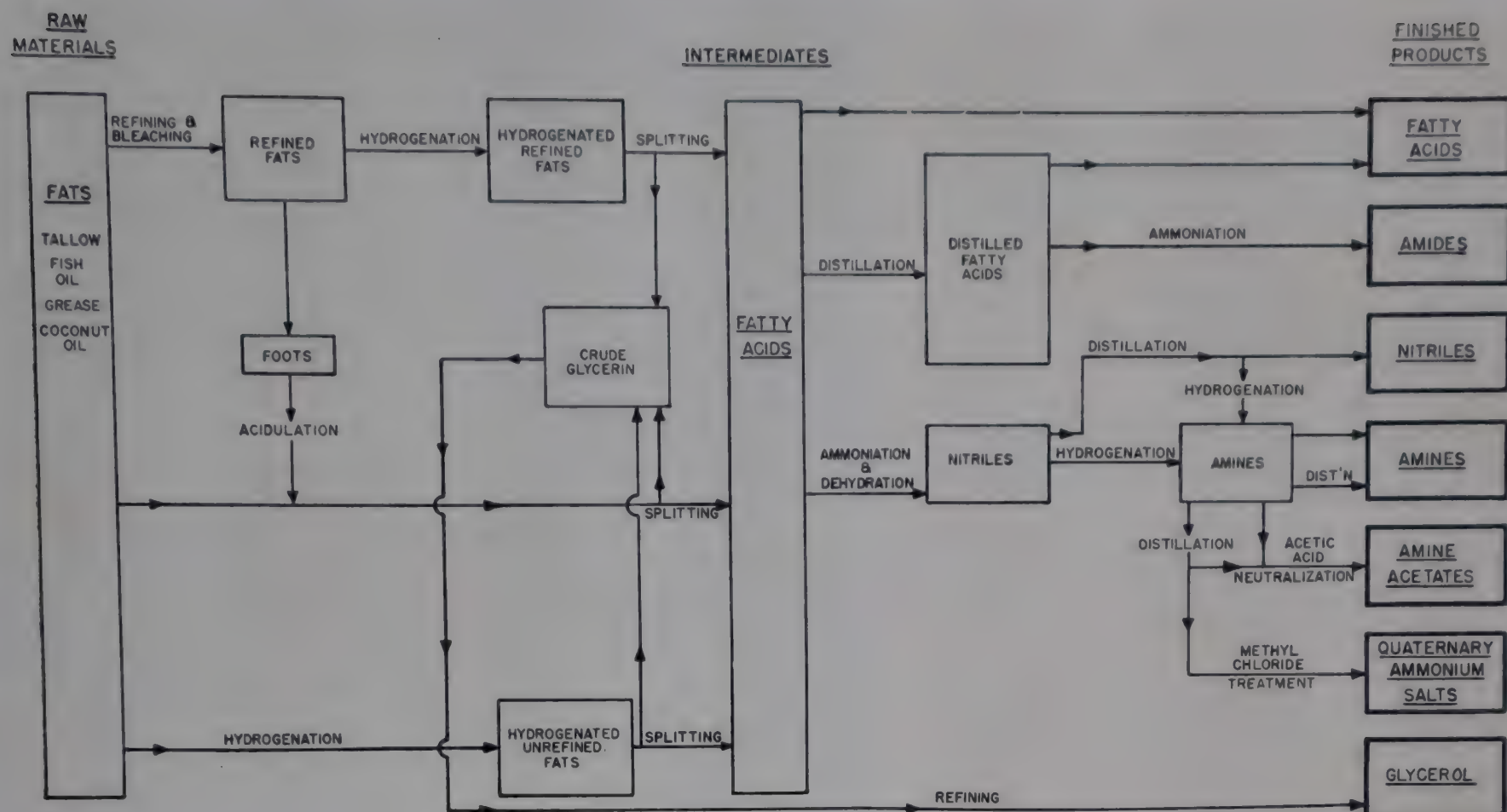
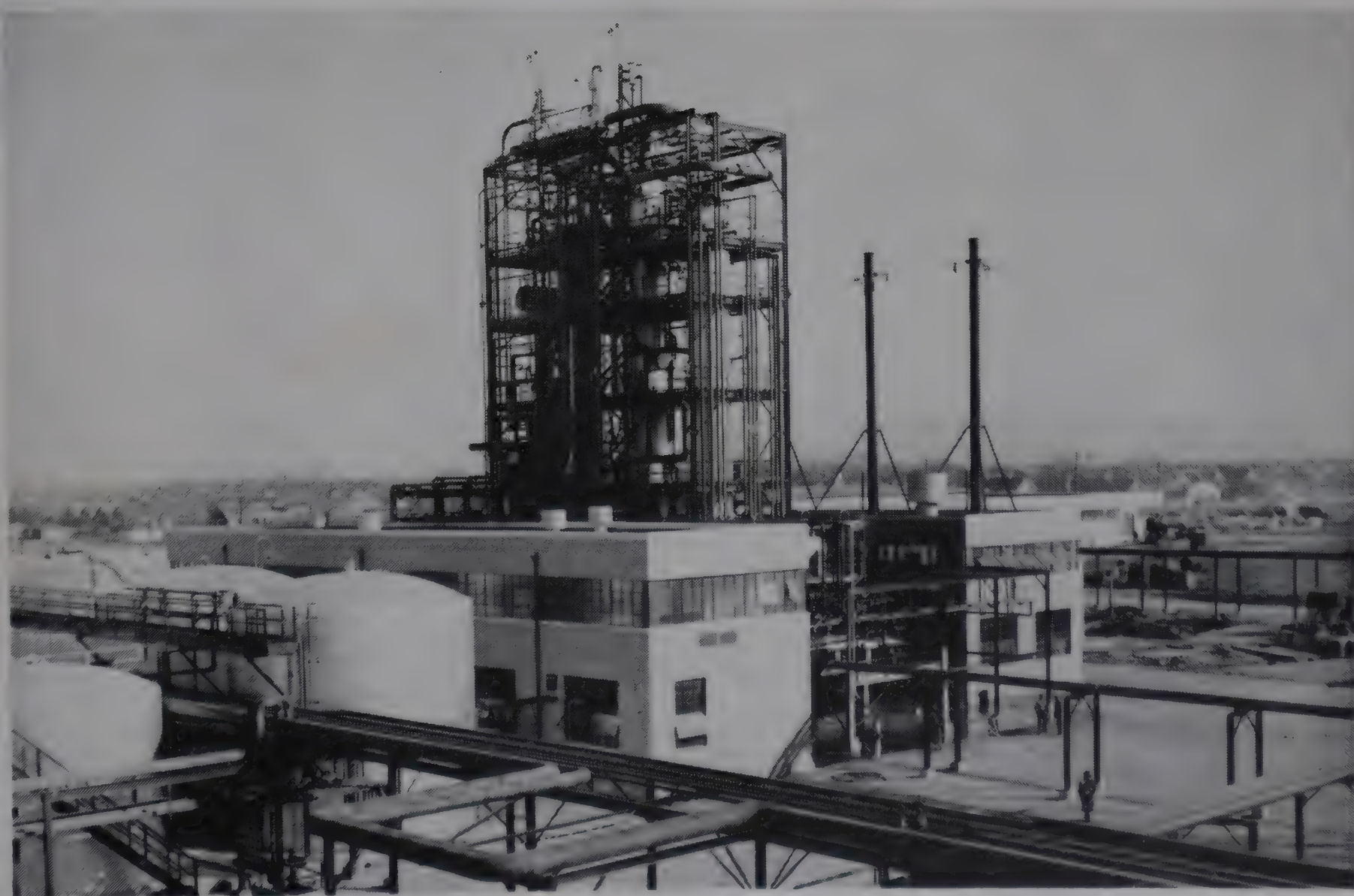


Figure 4. Chemical Flow Sheet

◆ ◆ ◆ ◆ ◆



Still Towers, Pump House, and Storage Tanks (left)

merely as acids of given carbon numbers of the unsaturated series and one product is stated to be a mixture of approximately 90% unsaturated C_{30} acids with three to four double bonds.

The lower homologs, of eight or ten carbons, or their derivatives are used in the manufacture of essences, perfumes, flavors, plasticizers, disinfectants, mineral concentration systems, anti-foaming agents, dyestuffs, pharmaceuticals, high boiling solvents, and plasticizers for lacquers, gums, plastics, waxes, and resins, and as intermediates in many other compounds. Proceeding upward by two carbons, the acids find many of the same uses and are used particularly in alkyd resin manufacture. In addition they go into detergents and wetting agents. The next higher find more uses in cosmetic and shaving creams and soaps and in metallic soaps. The latter are used in rubber and grease compounding, synthetic resins, and paints. The fatty acid which is mostly palmitic acid is used in plastics, salves, cosmetics, wetting agents and detergents, and as a raw material in other syntheses. The acid which is primarily stearic is used in metallic stearates, creams, shaving soaps, rubber compounding, pharmaceuticals, hard greases, and cosmetics.

The mixture of oleic and linoleic is used in gel soaps, special lubricants, oil emulsions, mineral concentration aids, alkyd resins, and as emulsifying, wetting, and penetration agents in the leather, textile, and related industries. The residues, which are called stearine pitches, are useful in paints of red or black color, insulating compounds, mastic flooring, and inks. The highly unsaturated mixtures are particularly valuable in making quick-drying paints and varnishes.

Amides. The amides, sold under the trade-mark Armids, are also mixtures and are classified by mean molecular weights. These weights vary, most of them being between 200 and 300. They are neutral, oily, or waxlike materials of fairly high melting point, insoluble in water, and of low solubility in most solvents at room temperature. Above their melting points they are appreciably soluble in organic solvents. They are used as tack-reducing agents in rubber and resin coatings, and to improve the slip and gloss of inks. They are also used as mutual solvents for incorporating waxes into resins and as starting materials for the preparation of water repellents and softening agents.

Nitriles. Mixtures of the fatty nitriles are sold with mean molecular weights ranging from 181 to 265. They are given the trade-mark Arneels. They are liquids or soft solids, insoluble in water, but soluble in most organic solvents and are strong solvents for many organic materials including polymers. They are employed as plasticizers for synthetic fibers, lubricants in yarn spinning, in industrial mineral concentration, and as starting materials for the synthesis of textile water repellents.

Amine Acetates. The amine acetates, under the trade-mark Armacs, are sold in mixtures with mean molecular weights ranging from 250 up to 365. They are solid or semisolid materials which are soluble or dispersible in water and in a variety of organic solvents. They are cationic surface active agents.

Quaternary Ammonium Salts. These compounds, marketed under the trade-mark Arquads, are produced in mixtures of mean molecular weights ranging from 264 to 585. They are dispersible in water or alcohol and those of higher molecular weight in some organic solvents. They are cationic surface-active agents and possess strong bactericidal and fungicidal activity.

The acetates and quaternary salts have some similar uses—for example, in preparing cationic softening agents, dyeing assistants, and other textile auxiliaries. In industrial mineral concentration, both are used on nonmetallic and metallic oxides and some sulfide minerals; they can be used to produce "soft" pigments; they are used also in making cationic oil emulsions

which are substantive to textiles, metallic, and siliceous surfaces, and to inhibit corrosion by acid solutions.

The quaternary salts have been applied as antistatic agents for plastics or textiles.

Properties, reactions, and uses of all these products are discussed in a technical bulletin (2E).

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AMYL COMPOUNDS FROM PENTANE

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GORDON C. INSKEEP

Associate Editors

in collaboration with

LESLIE GILLETTE AND
J. FRANK PRICE

Sharples Chemicals, Inc., Wyandotte, Mich.

Standard Solutions (lower left) Are Used by the Operator in Control of Amyl Acetate Column at the Sharples Wyandotte Plant

THE production of synthetic organic chemicals derived from petroleum sources is one of the largest fields in the chemical industry today. The mid-continent gas fields are the source of several raw materials used in the production of many useful products. The pentanes, which are removed from natural gas by fractionation, are the raw materials from which a large group of amyl compounds are synthesized by Sharples Chemicals at its Wyandotte, Mich., plant. The production statistics for amyl acetate and amyl alcohol from all sources are shown in Table I.

Development of the present industrial process for synthesis of amyl compounds was stimulated by two related findings in the early 1920's. Ayres found that when the hydrolysis of amyl chloride was carried out in the presence of a dispersing agent, such as sodium oleate, there was a marked reduction in the percentage of the chloride which was dehydrochlorinated to amylenes (4). There was a corresponding increase in the yield of amyl alcohols. In addition, there was developed a vapor-phase method for the chlorination of hydrocarbons which was more satisfactory with respect to yield of the desired products and also reduced the explosion hazard. Several patents were later granted to Ayres (2, 3) for this type chlorination.

SHARPLES HISTORY

The Ayres features were incorporated into the process by the Sharples Company and a pilot plant was built in Texas. This plant was operated only long enough to prove the superiority of the newly developed techniques. The rising demand for high boiling lacquer solvents to supply the expanding automobile industry indicated a need for a full scale industrial plant. Fusel oil and fusel oil acetates were being demanded by the lacquer industry but could not be obtained in sufficient quantities. Fusel oil was obtained as a by-product in the ethyl alcohol fermentation.

Kirkpatrick has pointed out the economic aspects considered in selection of a site for this new plant (9). A survey by the Sharples Company in 1925 and later an independent but confirmatory investigation by E. B. Badger and Sons recommended location at Belle, W. Va. This was near a casing-head gas source and was near enough to eastern and central United States distribution centers to balance the problems of raw materials and distribution satisfactorily. Caustic and chlorine were readily available from the Belle Alkali Company. Ground was broken for this plant in March 1926 and amyl alcohol was being produced there by December of that year.

TABLE I. AMYL ACETATE AND AMYL ALCOHOL PRODUCTION^a

Year	Amyl Acetate, Pounds	Amyl Alcohol, Pounds
1935	10,322,902	11,002,677
1936	10,222,991	11,473,212
1937	^b	14,205,997
1938	5,828,497	9,096,977
1939	^b	^b
1940	^b	^b
1941	4,853,000	^b
1942	^b	14,426,000
1943	11,499,000	14,256,000
1944	15,088,000	18,527,000
1945	15,589,000	13,773,000
1946	10,564,000	15,475,000
1947	12,981,000	17,728,000

^a U. S. Tariff Commission reports.^b Reliable data unavailable.

The hydrolysis was run batchwise at the beginning. The sodium oleate remained in the reactors; the raw materials were pumped in, agitated, and distilled off. The operation was converted to a continuous process in March 1928 with the result that the yield from the chloride to alcohol rose to 60% and eventually to 67%; this was with continuous hydrolysis but batchwise distillation.

The conventional method of esterification was not found satisfactory for the production of amyl acetate. Accordingly, Sharples set about studying the acetylation of amyl alcohol. By March 1927 the present method for introduction of the catalyst and flashing of the alcohol had been developed and was incorporated into a process for the manufacture of the ester.

The construction and operation of the Belle plant has been discussed previously in the literature (1, 5-7).

A favorable arrangement with the Pennsylvania Salt Company made a move to Wyandotte, Mich., attractive for the Sharples organization. Land was available adjacent to the Penn Salt plant and contracts for chlorine, caustic, and some utilities were worked out.

In the fall of 1932, dismantling of the Belle plant was begun. Actually, this was a meticulous project. By scheduled shutdown of the various units it was accomplished with little interruption of customer's supplies. Each piece of equipment, from large columns to small sample valves, was carefully marked and cataloged to simplify the job of reassembly. The equipment, housed in new quarters at Wyandotte, was back in operation by March 1933.

Although refinements have been made in the field of instrumentation and some changes in materials of construction, the present operation of the chlorination, hydrolysis, and acetylation units at Wyandotte is basically the same as at the original Belle plant.

Additional amyl derivatives of the chloride and alcohol are now being made at the Wyandotte plant (8) and are described in this article.

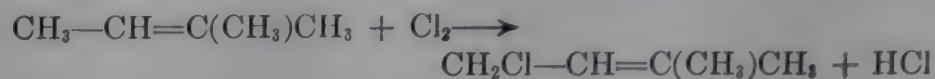
FUNDAMENTAL CHEMISTRY

The fundamental chemistry related to these processes is relatively simple. The chlorination of pentane is carried out in the vapor phase because higher yields to the primary chlorides are obtained. Also, the vapor-phase chlorination affords more control over the formation of dichlorides. The principal reaction in this chlorination of pentane proceeds with the formation of amyl chloride and hydrogen chloride



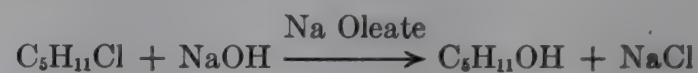
During the rectification of the amyl chlo-

rides the 2-me-2-chlorobutane or the 3-me-2-chlorobutane may decompose to form 2-me-2-butene or 3-me-1-butene. These olefins can be recycled to the chlorination step and under the conditions used, in the vapor phase at high temperature and under pressure, will chlorinate rather than add chlorine to the double bond

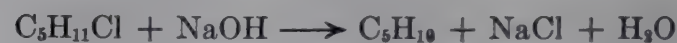


Thus the mixed chlorides will contain all the possible isomers of normal and isopentane as well as some unsaturated amyl chlorides.

The hydrolysis of the amyl chlorides is carried out in the presence of sodium oleate using aqueous sodium hydroxide. The sodium oleate may act either to emulsify the amyl chloride in the aqueous sodium hydroxide solution, or it may react with the amyl chloride forming amyl oleate which in turn is hydrolyzed by the aqueous sodium hydroxide. Since amyl oleate has been isolated from the reaction, it is evident that the hydrolysis proceeds, at least partially, in this manner



During this hydrolysis, the amyl chlorides are also dehydrochlorinated by the sodium hydroxide solution yielding the various isomeric ptenenes



The unsaturated amyl chlorides hydrolyze either rapidly or with difficulty, depending on the position of the chlorine atom relative to the double bond. The allylic-type amyl chloride hydrolyzes quite rapidly whereas the vinyl type goes through the hydrolysis step largely unreacted

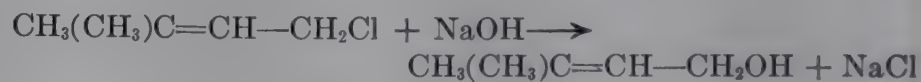


Table II gives a typical composition of crude amyl alcohol, as determined by infrared analysis.



Coal Fired Pipe Still Reactor

Surrounding barricade can be blanketed by steam in emergency

Amyl alcohols are esterified with acetic acid in the presence of sulfuric acid catalyst to yield amyl acetate and also some by-product pentenes

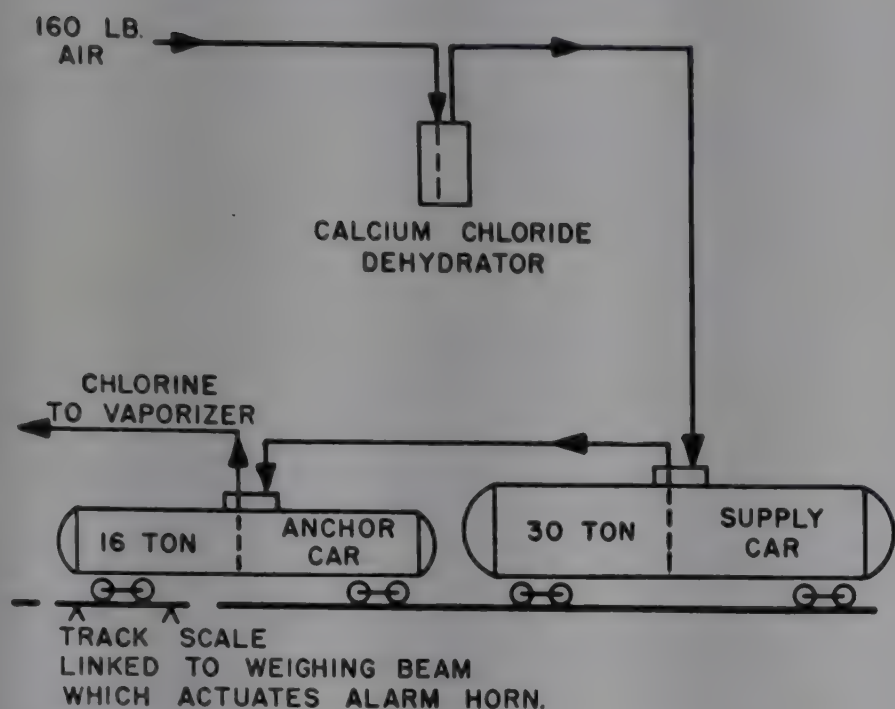
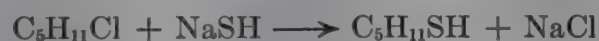


Figure 1. Chlorine Unloading Station

The pentenes are used in alkylating phenol and naphthalene to form the corresponding amyl derivatives



Amyl mercaptans are formed through the reaction of sodium hydrosulfide with amyl chloride in the presence of a mutual solvent



Amyl sulfide and amyl disulfide are also formed in this reaction as by-products



Products and Their Uses. The mixture of most of the theoretically possible isomeric chloropentanes of *n*-pentane and isopentane obtained from the vapor-phase reaction is marketed as mixed amyl chlorides. It is used in the synthesis of other amyl compounds and as a solvent in the formulation of synthetic rubber cements. In some alkylation reactions the primary isomers are more desirable; for these reactions a fractional distillation is used to produce mixed primaries which are available at a slightly higher price.

Dichloropentanes produced are a mixture of about 40% true amylene dichloride and 60% a mixture of most of the other dichloro derivatives of both normal and isopentane. This product has found use as a solvent, insecticide, soil fumigant, and oil additive. It is also used in the formulation of dipping cements for synthetic rubbers of the Buna N type. Dichloropentanes are one of the lowest priced chlorinated solvents now commercially available.

Hydrolysis of the chloride yields the alcohol. Sharples produces commercially only the alcohols containing five carbon atoms in the molecule. One commercial product is a mixture of the isomers (10); it contains six of the possible seven isomeric amyl alcohols but is predominantly composed of the three primary alcohols. This product is used as a latent solvent in the formulation of nitrocellulose lacquers and as a solvent for urea-

formaldehyde resins. It has been used successfully as the volatile portion of hydraulic fluids, and recently in antibiotic recovery as an extractant.

Primary *n*-amyl alcohol, isobutylcarbinol, *sec*-butylcarbinol, diethylcarbinol, and *tert*-amyl alcohol are separated by the fractional distillation of the crude amyl alcohols. All the isomers are used in various organic syntheses. Diethylcarbinol is used in the manufacture of flotation agents for nonferrous ores.

By esterification of amyl alcohol with acetic acid, Sharples produces a mixture of the isomeric amyl acetates (11). Large volumes of acetate are used as a penicillin extractant. It is also used in nitrocellulose lacquer formulations, and small quantities are used in the food industry as a flavoring agent.

The amyl chlorides are reacted with sodium hydrosulfide to give a mixture of amyl mercaptans (13) which is used as a fuel gas warning agent; one pound per million cubic feet of gas is the usual concentration.

Amyl mercaptan is a mixture of the various amyl isomers and can be used as a starting material in the synthesis of organic sulfur compounds.

Amyl sulfide is a yellow liquid having the amyl group present in its isomeric forms. It is used in the preparation of sulfones, sulfoxides, and other organic sulfur compounds through addition reactions.

Although Sharples has been producing amylphenols since the early 1930's, until just recently the amyl group present was either wholly or predominantly the tertiary isomer. The commercial scale production of the secondary amylphenols by reaction of the normal pentenes has been initiated by Sharples in the past 5 years.

p-tert-Amylphenol (12) is used in the preparation of pale-colored, light-stable, oil-soluble resins and also as an intermediate for pharmaceuticals.

TABLE II. COMPOSITION OF CRUDE AMYL ALCOHOL

Component	Formula	Boiling Point, ° C.	Percentage
2-Me-2-butanol	$(CH_3)_2COHCH_2CH_3$	101.8	6.0
2-Pentanol	$CH_3(CH_2)_2CHOHCH_3$	119.3	25.1
1-Pentanol	$CH_3(CH_2)_3CH_2OH$	138.0	25.5
3-Me-1-butanol	$(CH_3)_2CHCH_2CH_2OH$	132.0	11.9
2-Me-1-butanol	$CH_3CH_2CH(CH_3)CH_2OH$	129.5	16.8
3-Pentanol	$(CH_3CH_2)_2CHOH$	115.6	9.4
3-Me-2-butanol	$(CH_3)_2CHCHOHCH_3$	112.0	2.2
2-Butanol	$CH_3CH_2CHOHCH_3$	99.5	1.2
2-Me-1-butene-3-ol	$CH_2=C(CH_3)CHOH-CH_3$	116.6	1.3
2-Me-2-butene-1-ol	$CH_3CH:C(CH_3)CH_2OH$	139.4	0.7

Two isomeric *o*-amylphenols are produced; in one the amyl group is predominantly tertiary and in the other predominantly secondary. Both products can be used as intermediates for the synthesis of other compounds where specific properties are required. Both are effective antiskinning agents for paints and varnishes. Diamylphenol is also used for this purpose; the choice of agent depends on the nature of the other components.

Mono-, di-, and polyamyl naphthalenes also are marketed by Sharples (14). These are somewhat viscous liquids resembling lubricating oil in appearance and are used as plasticizers, heat transfer media, solvents, and as starting materials in the manufacture of surface-active agents.

PRODUCTION OF AMYL COMPOUNDS AT SHARPLES WYANDOTTE PLANT

Raw Materials. Pentane is received from West Virginia, Oklahoma, and Texas. Its composition varies, according to specification, from a high *n*-pentane to a high isopentane content. Most of the product contains approximately equal proportions of the straight- and branched-chain isomers.

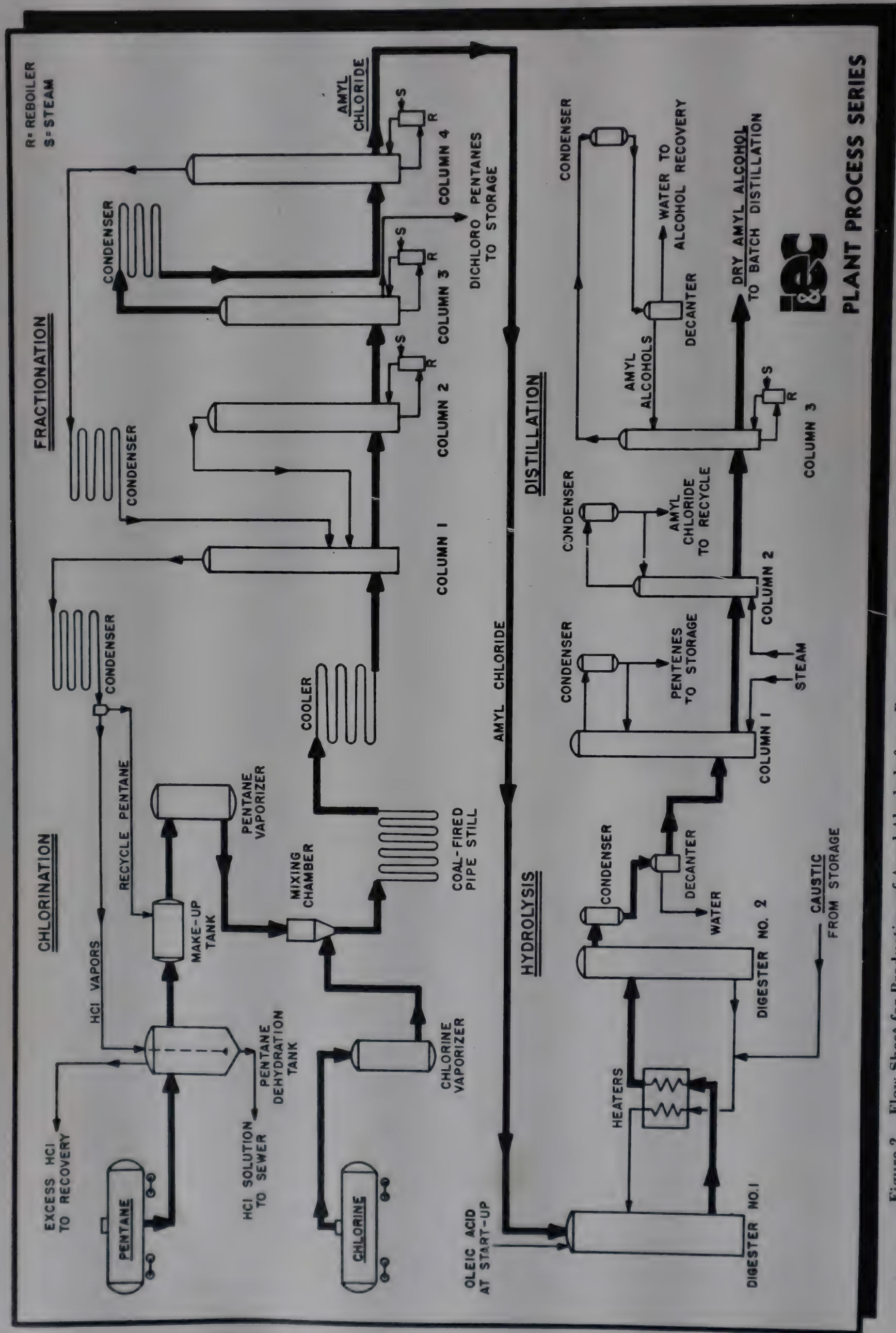


Figure 2. Flow Sheet for Production of Amyl Alcohols from Pentane at Wyandotte, Mich., Plant of Sharples Chemical Company



Tertiary Amylphenol Unit Showing Alkylation and Digestion Autoclaves

The pentane is shipped in standard steel tank cars having a bottom valve. The hydrocarbon is pumped from this bottom valve by means of explosion-proof centrifugal pumps, through a flexible metal hose, to storage tanks to which the tank cars are also connected by means of pressure equalizer lines. The tanks are 27,000-gallon horizontal units of welded construction.

Chlorine is received from Pennsylvania Salt Manufacturing Company, located just across the highway, in 30-ton tank cars. A full car, in addition to that being unloaded, is maintained at the unloading station. Figure 1 shows the station schematically. The liquid chlorine is forced out of the car by compressed air and is transferred to a standby, or anchor car. In order to maintain anhydrous conditions, this air is previously dried by passing it through calcium chloride traps. The anchor car is a 16-ton tank which sits on half-track scales (2A).

A small mercury switch is attached to the weighing beam. After the supply car has gone empty and the weight of the anchor car starts to decrease, the beam drops actuating an electric horn. The operator then knows it is time to change over supply cars. He throws a manual switch which turns off the horn and sets the circuit to contact again when the weight of the tank starts to increase. When he hears the alarm again, he knows that the anchor car has started to fill. Turning off the alarm automatically sets the circuit for contacting when the weight starts to fall; the cycle is then repeated. In this system the anchor car serves as a surge tank between the incoming chlorine cars and the process itself; there are no other chlorine storage facilities.

Caustic is also received from Penn Salt. It is pumped underground from their plant, as a 35% solution of sodium hydroxide, to storage tanks where it is diluted with water to a 12% concentration.

Other important raw materials received by Sharples are shown in Table III.

The chlorination and hydrolysis operations are shown in Figure 2.

From the storage tanks, pentane for the process is pumped by positive pressure pumps to the dehydration tank, a 4500-gallon, upright, carbon steel, cone-bottomed tank with a 3-inch gas induction pipe entering the top and reaching to within 18 inches of the bottom. The induction pipe is blinded on the end and drilled with numerous holes. The dehydration tank is connected by a gravity flow line and also by a pressure equalization line to a 3000-gallon horizontal make-up tank.

About 3300 gallons of pentane are pumped to the dehydration tank and hydrogen chloride gas, a by-product of chlorination, is constantly bubbled in through the induction pipe. As it rises it absorbs any moisture present in the pentane and a dilute solution of hydrochloric acid collects in the bottom of the tank from which it is drained to the sewer at regular intervals. The excess hydrogen chloride gas passes out the top of the tank to the recovery unit; anhydrous pentane goes to the make-up tank.

Chlorination. From the make-up tank, which also receives recycle pentane, the anhydrous hydrocarbon is pumped by duplex pumps to a steam-heated vaporizer. The vaporizer is a shell-and-coil unit with steam in the shell. The vapors are carried through a 4-inch pipe to the mixing "throat," which is a modified Venturi mixing chamber. The mixer is made of cast steel.

During this time, liquid chlorine is passing through a similar shell-and-coil vaporizer which yields vapors at 140 pounds per square inch. The pressure is reduced by means of a control valve and the vapors pass through a flowmeter (10A) at about 80 pounds pressure. Gaseous chlorine flowing through the meter causes the piston to rise exposing calibrated orifices drilled in the cylinder wall thereby increasing the total effective orifice area; the rate of flow is indicated in the lower calibrated chamber containing a liquid seal of carbon tetrachloride. A pressure gage is tapped in directly on the meter, and both pressure and flow rate are manually controlled.

Chlorine vapors enter the throat through two lines; one of these is located on each side of the chamber just behind a narrow orifice through which pentane vapors enter. A pentane-chlorine ratio above the explosive limit is maintained at all times. The mixture of pentane and chlorine then flows to a pipe still-type reactor for completion of the reaction.

The pipe still consists of units of hairpin turns of 3-inch pipe. The upper end of each hairpin enters a horizontal header pipe. Each header receives eight hairpins. There are seven headers connected in series. The pipe still is heated by means of a coal-fired forced-draft furnace (7A) which is controlled by an automatic stoker. There is a gradation of temperature in the pipe still from about 120° at the entering end to 300° C. at the exit end.

From the pipe still the gases pass immediately to coolers to prevent the formation of excessive dichloropentanes. These coolers are a pair of units in parallel, each unit consisting of nine hairpin turns of 4-inch pipe, over which cooling water falls. The pressure at the feed throat carries through the pipe still. Cooling beyond the still aids in drawing the stream through. This exposed type cooler is used in the process because it makes immediate detection of any leaks possible. The conventional shell-

TABLE III. RAW MATERIALS RECEIVED

Material	Grade	Container
Pentane	Specially refined	Tank car
Chlorine	Anhydrous	Tank car
Caustic	35% NaOH soln.	Pipe line
Oleic acid	Red oil	Drums
Sulfuric acid (for acetylation)	c.p. 66° Bé.	Carboys
Sulfuric acid (for <i>tert</i> -amylphenol)	Technical 66° Bé.	Tank car
Acetic acid	Glacial	Tank car
Phenol	U.S.P.	Tank car
Sodium hydrosulfide	45% NaSH soln.	Tank car

and-tube cooler was originally used but minor leaks in any one tube would cause failure of the complete unit in a very short time by the formation of hydrochloric acid in the shell.

Fractionation. From the coolers, the product mixture which contains some liquid is passed to the fractionating columns, entering the bottom of column No. 1, a nine-plate unheated bubble-cap column. The overhead is hydrogen chloride and pentane. It passes through a water-cooled condenser consisting of nineteen sections of six hairpin turns each of 2-inch pipe feeding into a header; water flows over these pipes in a constant stream. The hydrogen chloride gas then passes to the dehydration tank previously described. All the chlorine is reacted in the pipe still. The excess pentane is condensed and runs by gravity to the make-up tank.

The bottoms from No. 1 column, consisting of amyl chlorides, dichlorides, and pentane, are pumped to No. 2 column which is a bubble-cap column with shell-and-coil reboiler. Pentane distills off the top of this column and is returned without condensing to the bottom of the first column. The bottoms of the No. 2 column are used as manually controlled feed to the third column.

The first two fractionators are under pressure controlled in the acid recovery plant. The last two columns provide essentially atmospheric fractionation.

Column No. 3 is a bubble-cap still with reboiler. The distillate consists of a mixture of amyl chlorides and a small amount of pentane. It passes through a ten-section condenser after which a stream is fed to column No. 4 and a portion returned as reflux. The bottom take-off is amylene dichlorides and is sent to storage.

Column No. 4 is a bubble-cap column with reboiler operated in the 85° to 90° C. temperature range. The distillate is pentane which is condensed and pumped to column No. 1. The bottoms are amyl chlorides which go to storage as finished product.

The condensers for columns 3 and 4 have vent lines to take off any hydrogen chloride still present. This gas is led to a scrubber which dilutes it and carries it to the sewer.

Hydrogen Chloride Reclamation. The hydrogen chloride gas, after passing through the dehydration tank, passes through a water-cooled condenser where almost all the pentane is condensed. The stream flows through receivers where the liquid pentane drops out and the acid gas continues to a vertical series of ceramic cells

(9A) where it is absorbed. The cells consist of hairpin turns of ceramic tubing. In one bank the units are 8 inches in diameter and 5 feet long, and in the other the units are 6 inches in diameter and approximately the same length. A slight vacuum is maintained in these cells by means of a compressor.

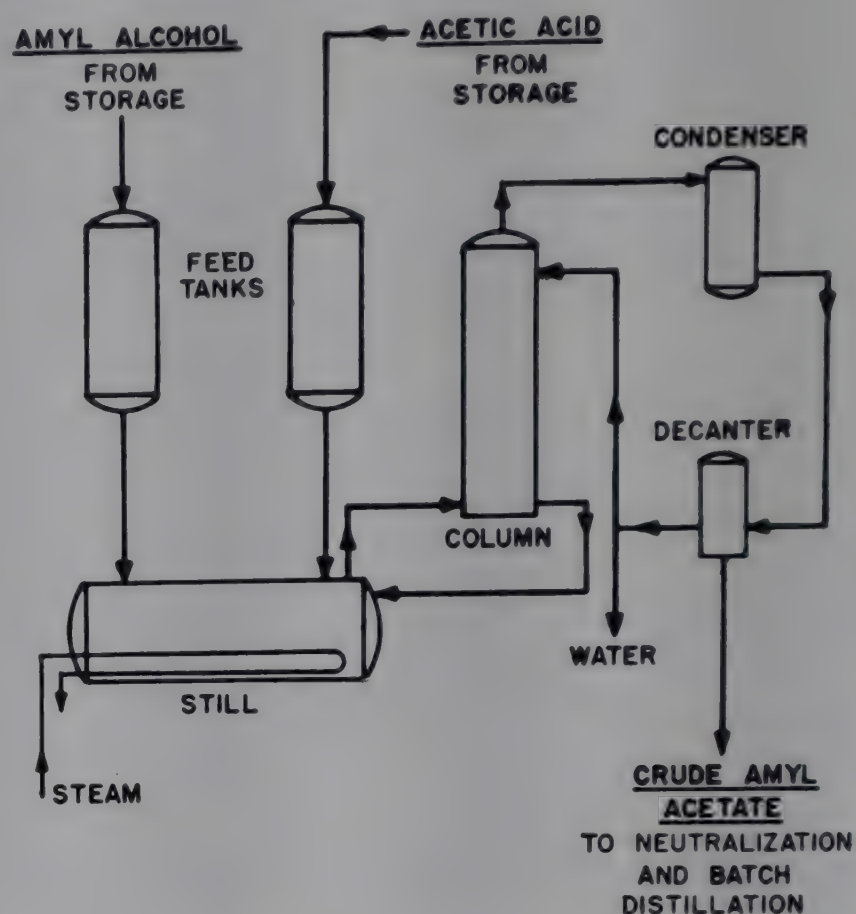


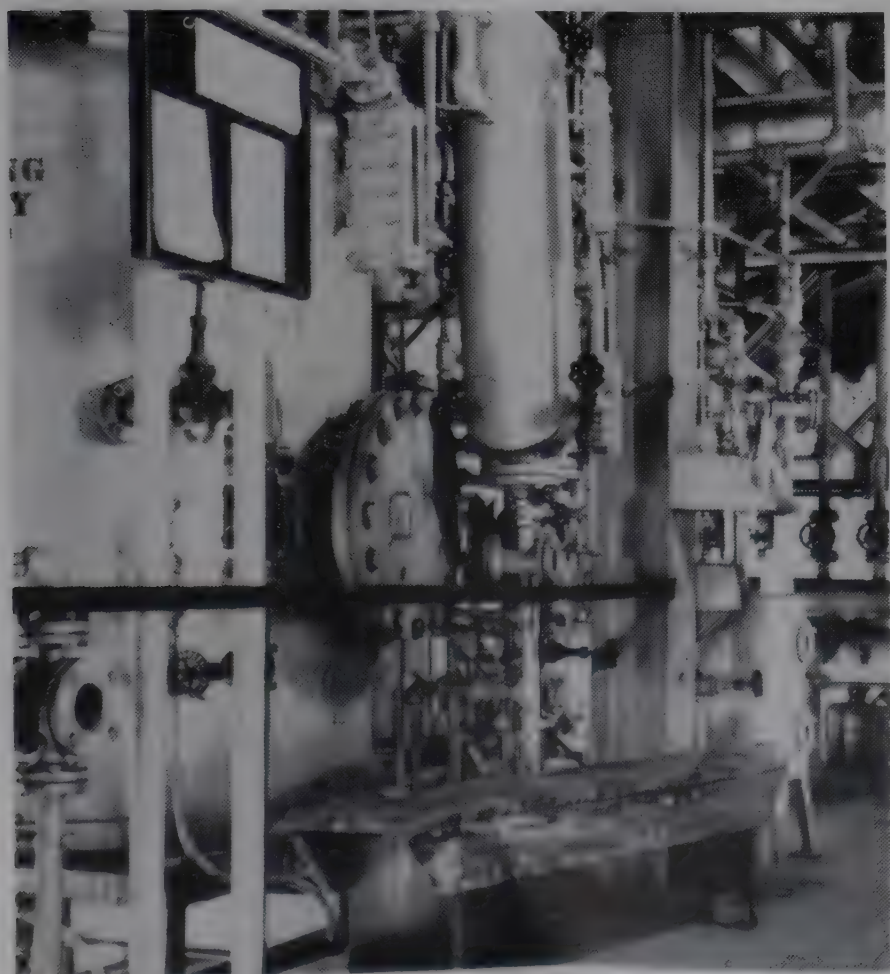
Figure 3. Flow Sheet for Production of Amyl Acetate

Hydrogen chloride enters the bottom of the series of 8-inch cells and is pulled upward by the vacuum to be met by a downward flow of water which absorbs most of it. The unabsorbed gas passes to the bottom of the 6-inch cell bank where the process is repeated. The 8-inch cell yields 22° Bé. hydrochloric acid, whereas the 6-inch cell gives a solution of 18° Bé. strength. The acid streams pass through decanters which are of particular value in the start-up, when some pentane condenses in the cold system. The pentane is held in the decanter and is flashed off by the hot acid solution which is formed. During the absorption process in the cells, residual pentane in the hydrogen chloride stream is vaporized by the heat of solution in the cells and passes out the top of the cells through a brine scrubber and a condenser to a receiver. Any uncondensed pentane goes through the compressor on the intake side and is discharged, under 60 pounds per square inch pressure, through a condenser into a receiver. Uncondensables are vented off through a valve, and the pentane is discharged to the make-up tank by the pressure.

The acid from the 6-inch-diameter cell bank is fed to storage by gravity as the take-off is several feet above the ground. The acid from the longer 8-inch-diameter cell bank discharges to a blow case from which it is transferred by air pressure to storage. About 98% of the hydrogen chloride formed is reclaimed in this system. A very pure grade hydrochloric acid is produced and is used exclusively in the food industry.

The brine used in the pentane scrubber is a 20% salt solution, containing about 0.5% sodium hydroxide, which is a by-product of the subsequent hydrolysis of amyl chloride. From the scrubber it is discharged to the sewer. The scrubbers are resin impregnated asbestos (6A) tanks packed with carbon Raschig rings.

Vents from all acid tanks, blow cases, and cars are connected to a water scrubber. The resultant scrubber solution, which is mildly acid, is run to the sewer, the contents of which are alkaline.



Decanters in Continuous Alcohol Fractionation

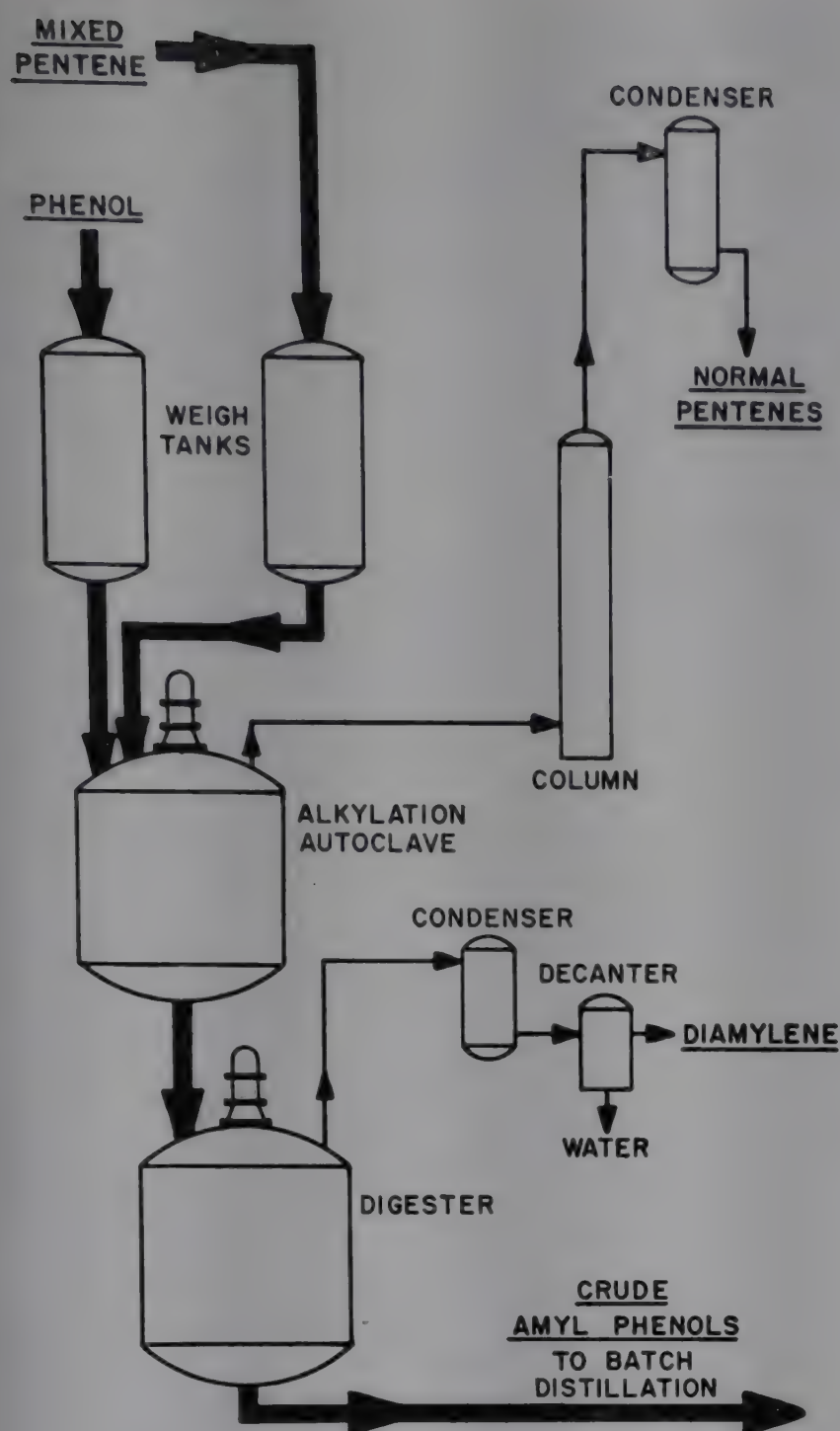


Figure 4. Flow Sheet for Production of Amylphenols

Hydrolysis. Amyl chloride (a mixture of primary, secondary, and tertiary chlorides) is transferred by positive displacement pumps from storage to weighing tanks. These are steel tanks of 1000-gallon capacity, set on scales. As the chloride still contains some traces of hydrogen chloride it is passed through a caustic scrubber before entering the digester. The scrubber is an unpacked tank. It is partially filled with 12% caustic from the regular supply, and the chloride is pumped into the bottom to rise through the caustic. The scrubbing solution is checked at intervals of approximately 3 hours. When its strength is reduced to 4% sodium hydroxide, it is drained and the solution replenished.

The hydrolysis of amyl chloride is carried out in a pair of digesters, which are steel reaction vessels without packing or agitation, insulated with 2-inch magnesia blocks. Digester 1 is filled, at start-up, with oleic acid, amyl chloride, and enough preheated 12% caustic solution to bring the entire reaction mixture to a sodium hydroxide concentration of 3%. The mixture flows from No. 1 through an outlet near the bottom which is controlled by a gate valve, through a heater, and into the top of digester 2. A stream is pumped by centrifugal pump from the bottom of No. 2, through another heater, and enters the top of digester 1.

The digester heaters are made of 2-inch pipe inside 3-inch pipe and are designed as parallel hairpin turns feeding into common headers. Because of its consistency, the reaction mixture is referred to as the "paste." The paste flows through the inner

tube. Feed enters the bottom header and the effluent mixture comes from the top header. The temperature in the digesters is regulated by automatic control of the steam pressure in the heaters within a range of $\pm 1^\circ \text{C}$.

Once this start-up has been effected, constant charging of amyl chloride is begun. The chloride enters digester 1 through a 1-inch-diameter pipe, 8 feet long, which is closed at the end and perforated with $\frac{1}{8}$ -inch holes to feed a spray of the chloride into the reaction mixture. There are sufficient holes to be equivalent to one and a half times the cross-sectional area of the inlet pipe.

Addition of caustic, at the suction side of the circulatory pump, is begun at a rate which will maintain a concentration of sodium hydroxide of not less than 0.5% in digester 2. The caustic passes through concentric tube preheaters which are heated by the condensate from steam traps.

The feed of both amyl chloride and caustic is regulated by means of pneumatic controllers (4A) which control the steam pressure operating the positive displacement pumps on both feed lines. The pumps operate with a steam pressure of about 150 pounds per square inch. Pressure in the digesters is limited by a pressure relief valve which blows into a condenser at the pressure limit. An alternate valve is maintained for checking purposes.

Product distills from a take-off line leading from the top of digester 2 to a shell-and-tube condenser in which cold water passes through the tubes. The alcohol mixture which contains amyl alcohol, amyl chloride, amylene, and water flows from the condenser through a decanter, where a major portion of the water is removed and sent to a stripper to recover the alcohol. At this point the organic portion of the reaction product mixture is only about 3% soluble in water and separation is relatively easy.

The residue, or bottoms, in the digester consists of a brine almost saturated with sodium chloride and containing about 0.5% sodium hydroxide. This is continuously drawn off the bottom of digester 2 through an automatic control valve (3A) which is regulated by the specific gravity differential between the effluent brine and the reaction mixture in the digesters. A check sample is constantly drained near the bottom of digester 2 within sight of the operator. The brine is milky, and the reaction mixture is dark. Visual indication is thus given if the brine level falls below the safe point. The brine sample is analyzed regularly by the operator to determine its alkalinity. The rate of caustic feed is based on the alkalinity of the brine. A very small make-up of oleic acid is added occasionally.

If all the chloride and alcohol were depleted during the hydrolysis there would remain a sticky mass which could not be pumped. As a safeguard, a sample is taken from the pump once every 2 hours; it is acidified and steam distilled to determine the amount of volatile material present. Another safeguard is a red light for which electrical contact is maintained by the brine under pressure. If the paste gets into the pressure tap, the small line plugs up; this reduces the pressure on the electrical contact and turns off the light.

The brine, which is drawn from digester 1, is discharged by digester pressure to a flash tank on the second floor, where the small amount of low boiling organic material contained is flash-distilled through a water-cooled condenser to a decanter and thence to a column. The brine then goes to storage tanks. Some of it is used to neutralize hydrogen chloride which comes off with pentane vapors from the hydrochloric acid unit.

The product which distills from the top of digester 2 is pumped from a receiver to a 26-plate bubble-cap column which is sparged with steam. This column operates under pressure of 26 pounds per square inch. The low boiling organic material which is flashed from the brine also goes to this column. The stream is introduced just below the middle of the column. Amylene is taken from the top of this column and passes through a shell-and-tube condenser. A portion is returned to the column as reflux,

and the remainder goes to a decanter from which water is separated and the amylene is sent to a receiver tank.

Amyl alcohol, amyl chloride, and water are taken from the bottom of the first column, where the liquid level is maintained by liquid-level (3A) control traps. The mixture is discharged by pressure to column 2, a 26-plate column, the stream entering about the middle. A sparge of steam is used to maintain the desired heat. Amyl chloride is taken from the top of the column through a condenser and partly returned to the column as reflux. The remaining portion of the stream flows to a decanter where water is separated and the amyl chloride flows to receivers; from here it is returned directly to the digester feed weighing tanks.

The alcohol and water are collected from the bottom of column 2 and passed through a coil-in-shell cooler, thence pumped centrifugally to a decanter. Water goes to the collection tank which receives all decanter water from this operation, and the amyl alcohol goes to column 3, which is called the dehydration column. This column has a steam heated coil reboiler. All water and a small amount of alcohol are taken off through the top of the column, through a condenser, and to a decanter. The alcohol collected from the decanter is returned to the column as reflux. From the reboiler, a stream of alcohol is taken through a coil cooler and is centrifugally pumped into 500-gallon receivers. After analysis it is sent to storage.

Alcohol Distillation. After the crude alcohol is collected in a storage tank it is rectified. The rectification still consists of a 6000-gallon steel kettle with a 26-plate bubble-cap column. There are two of these columns.

About 5500 gallons of alcohol are charged into the kettle, which is heated by means of a steam scroll. The distillate stream is passed through a decanter until it has become nearly dry. A distillation rate of about 1200 gallons per hour is then established. A small stream of alcohol is taken off and the remainder is returned as reflux until the stream is thoroughly dry. The take-off is then increased and the collection of distillate fractions is begun. Alcohol specifications are shown in Table IV.

TABLE IV. AMYL ALCOHOL SPECIFICATIONS

	Pentanol No. 27	<i>tert</i> -Amyl Alcohol	Normal Amyl Alco- hol
Color	Water white	Water white	Water white
Specific gravity, 20/20° C.	0.81-0.82	0.81-0.82	0.82
Acidity, mg. KOH/g. maximum	0.06	0.06	0.06
Water content	None	None	None
Distillation, ° C.			
Initial, min.	112.0
Not more than 5% below	118.0
Not more than 50% below	125.0
Not more than 85% below	130.0
Final, max.	140.0
95% between	...	98.8-103.8	134.5-138.5

The residue, amounting to about 2% of the total charge, is redistilled to obtain amyl ether, which is collected over a distillation of 165° to 199° C. The remaining residue, which is principally oleic acid, is discharged as waste products.

Amyl Acetate. A flow sheet for the acetylation reaction is shown in Figure 3. Amyl acetate is prepared in a 4000-gallon copper reaction kettle to which is attached a bubble-cap copper column, 4 feet in diameter. Amyl alcohol and glacial acetic acid (approximately 99%) are added with enough water to give an acetic acid concentration of approximately 40% in the total mixture. Two per cent, by weight, of concentrated sulfuric acid is added.

Steam, at 40 to 60 pounds pressure is passed through the heating coil to begin distillation. About 5% acetic acid is initially carried over in the stream. The entire product is fed back as reflux until the acetic acid content is 0.5% or less. The take-off is then opened to the receivers to give a 3:1 reflux ratio and the product is collected in receivers. The addition of alcohol is then



Pentane Dehydration Tank, Product Storage Tanks in Foreground

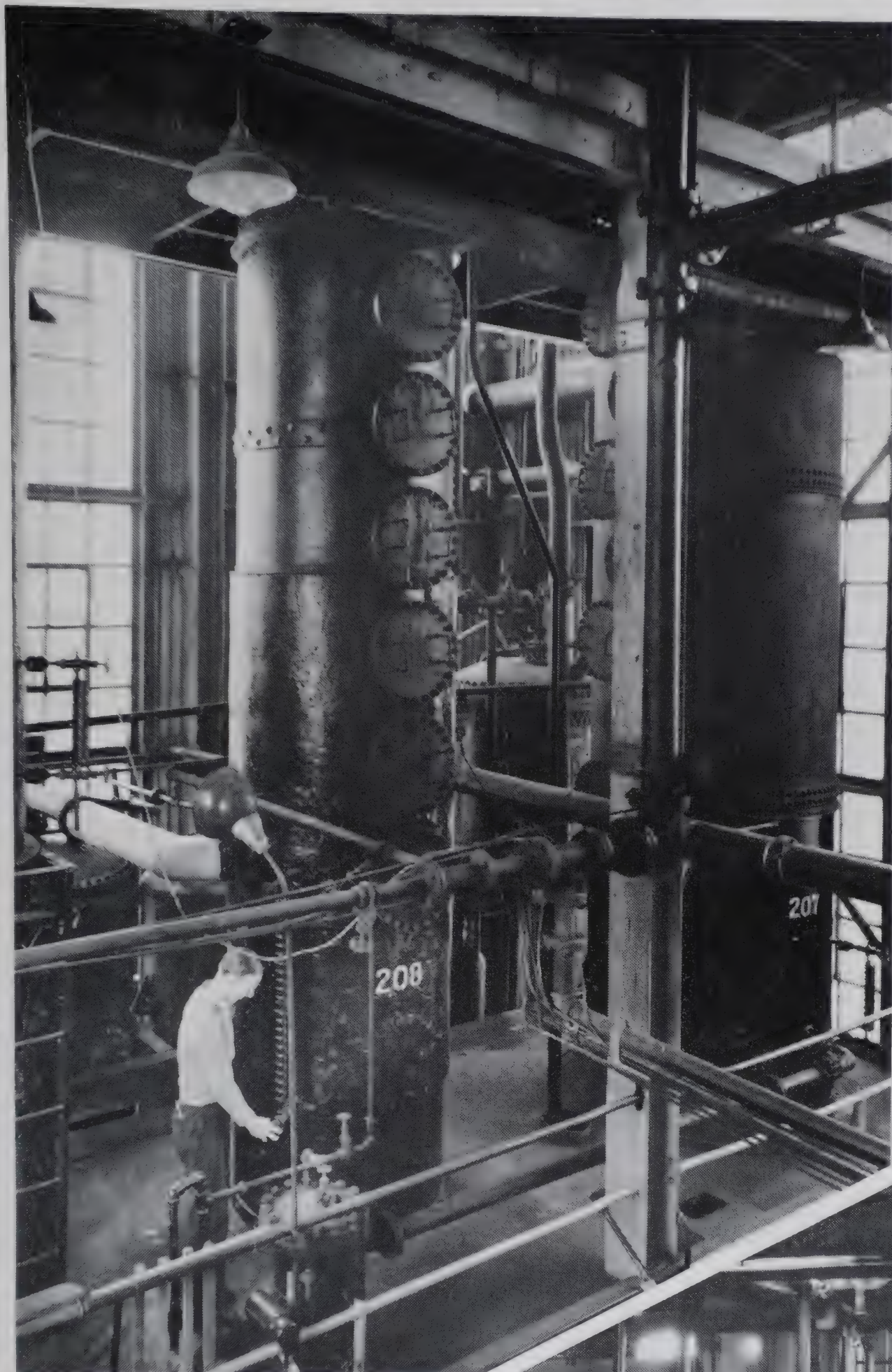
begun and is continued at a rate to maintain the liquid volume of the still. Acetic acid is added to maintain the 40% concentration.

The water resulting from the esterification reaction must be taken off. The distillate from the still passes through a tube-and-shell condenser and into a decanter. One side stream is taken from the decanter as crude acetate and another as water. A portion of both the water and the acetate is refluxed to the column.

The crude acetate is collected in receivers where it is held until an analysis has been made. It then flows to the neutralizing tank where sodium carbonate solution is added to produce neutrality. From the neutralization tank, the product is pumped to a storage tank which feeds the rectification still. After analytical checking, the batch is fed to a 6000-gallon carbon steel batch still with bubble-cap column. The first product from the still is the amylene produced by decomposition during the process. The next product is water which goes to a decanter for separation of the crude acetate. A cut is then taken which consists of about 23% acetate and the remainder alcohol. This is recycled back to acetylation. An intermediate cut follows. This is about 60% acetate with alcohol which is returned to the crude neutralizing tank. The relative volumes of these heads cuts depend on the ester content of the crude ester charged. The remainder of the batch comes off as amyl acetate product containing about 87 to 88% amyl acetate in amyl alcohol. All cuts are collected through a copper shell-and-tube condenser. There is no residue in the still. The final product is blended with amyl alcohol to produce a consistent 86% concentration of acetate.

Water fractions from this distillation are sent to a storage tank. When a sufficient quantity has accumulated, it is distilled through a pot still to recover the acetate, which then goes to the acetate rectification still.

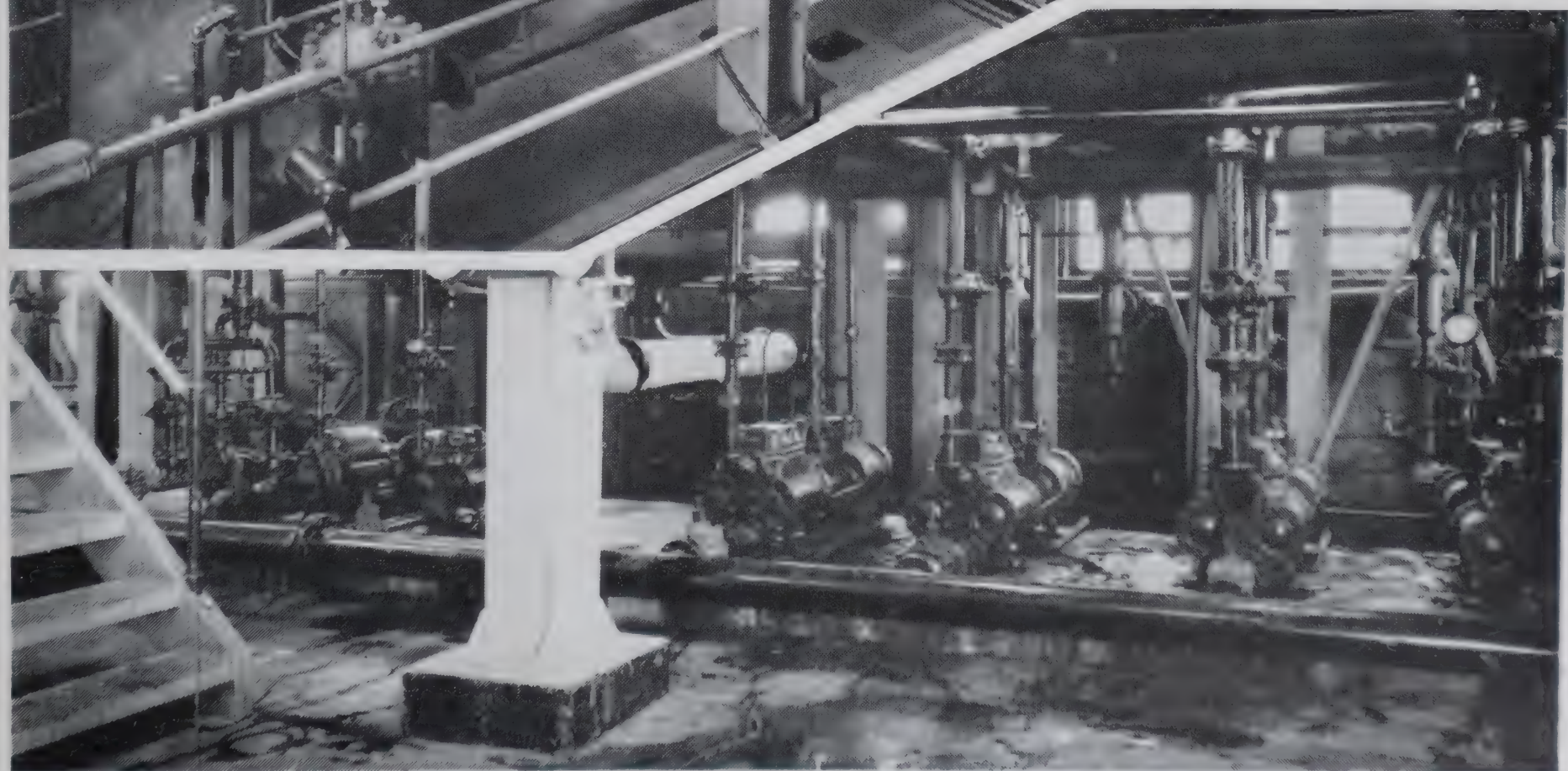
Tertiary Amylphenols. The pentenes produced as a by-product in the hydrolysis of the amyl chlorides contain all the isomeric pentenes. The two tertiary pentenes, 2-methyl-2-butene and 2-methyl-1-butene, are preferentially reacted with phenol to form the tertiary amyl phenols. This process is shown in Figure 4. Phenol is alkylated with the tertiary pentenes in the presence



Fractionating Towers Following
Chlorination Reaction



Pentane Feed Pumps
on Lower Level in
Chlorination Unit



of sulfuric acid. The reaction is carried out at 50° C. in a glass-lined reactor (8A). The unreacted normal pentenes are removed from the reaction mass by distillation after the addition of water to inactivate the sulfuric acid. The aqueous layer is decanted from the alkylate and the latter is transferred to a digester. After digestion, the crude containing a preponderance of *p*-*tert*-amylphenol is neutralized with dilute caustic solution. This neutralized crude is then sent to a batch vacuum still that separates the isomeric monoamylphenols and the diamylphenol. The still is equipped with a two-stage steam ejector which provides 29 inches of mercury vacuum.

Secondary Amylphenols. The unreacted normal pentenes from the *tert*-amylphenol process are reacted under more drastic conditions to form *sec*-amylphenols. The reaction temperature is 100° C. and the pressure above 150 pounds per square inch.

The normal pentenes containing only traces of isopentenes are pumped into an autoclave which contains molten phenol and a catalyst. The rate of the pentene feed is regulated by the pressure in the autoclave. After the desired degree of alkylation is reached, the neutralized crude is pumped to intermediate storage and then to a high temperature vacuum still. This still is provided with the same type two-stage ejector but is operated at a kettle temperature in excess of 200° C. A biphenyl ether heat transfer medium (1A) is circulated in the heating coils. The ortho-, para-, di-, and poly-*sec*-amylphenols are separated in this still.

Amylnaphthalenes. The amylnaphthalenes are produced by alkylating naphthalene with the unreacted normal pentenes from the amylphenol process and with amyl chloride using aluminum chloride in the Friedel-Crafts reaction (Figure 5). Mixed amyl chlorides are mixed with molten naphthalene and the system is dehydrated azeotropically by distilling off a portion of the amyl chloride. Aluminum chloride is then added to the dry mixture, and the temperature is increased. When most of the hydrogen chloride is vented off through a scrubber, more aluminum chloride is added and then normal pentenes are pumped in at a rate to maintain the reaction mass at about 180° C. The crude reaction

TABLE V. MATERIALS OF CONSTRUCTION

Product or Operation	Equipment	Material	Remarks
Chlorination	Pentane dehydrator	Monel-clad cone	Aqueous HCl present
Chlorination	Venturi mixer	Cast steel	Anhydrous conditions
Chlorination	Pipe still	Carbon steel	Anhydrous conditions
Chlorination	Fractionating columns	Carbon steel	Anhydrous conditions
HCl recovery	Gas absorbers	Ceramic	Aqueous HCl present
HCl recovery	Decanters	Haveg	Aqueous HCl present
HCl recovery	Blow cases	Rubber-lined	Aqueous HCl present
Pentane recovery	Scrubbers	Haveg	Caustic and brine used to neutralize HCl
Hydrolysis	Digesters	Carbon steel	Alkaline material at high temperatures
Alcohol distillation	Kettles and columns	Steel	Neutral conditions
Esterification	Kettle and column	Copper	Acetic acid present
Ester distillation	Kettle and column	Steel	Neutral conditions
<i>tert</i> -Amylphenol	Reactor	Glass-lined	Phenol present
<i>tert</i> -Amylphenol	Still	Steel	Crude is neutralized
<i>tert</i> -Amylphenol	Condenser and subsequent lines	Stainless steel	Product is discolored by iron
<i>sec</i> -Amylphenol	Autoclave	Nickel-clad	Acidic conditions at high temperatures
Amylnaphthalenes	HCl scrubber	Wood	Aqueous HCl present
Amyl mercaptan	Autoclave	Inconel-clad	Sulfides and chlorides present

mass is then pumped to a neutralizer where dilute caustic is added and the aluminum chloride complex is decomposed. The unreacted amyl chloride and pentene are then distilled off. The aqueous layer is separated from the crude amylnaphthalenes which are dried in an aerator. The dried crude is filtered and then fractionated in a high temperature vacuum still. The mono-, di-, and polyamylnaphthalenes are separated by this fractionation.

Amyl Mercaptans. The amyl mercaptans are produced by reacting mixed amyl chlorides with an aqueous solution of sodium hydrosulfide in a mutual solvent, ethanol (Figure 6). Amyl chloride, aqueous sodium hydrosulfide, and ethanol are charged to an autoclave; the total charge is 650 gallons. This mixture is reacted at 140° C. and 325 pounds pressure for 5 hours. The



Weigh Tanks for Amyl Chloride and Caustic Fed to Digesters; Acetylation Kettle at Right

CORROSION

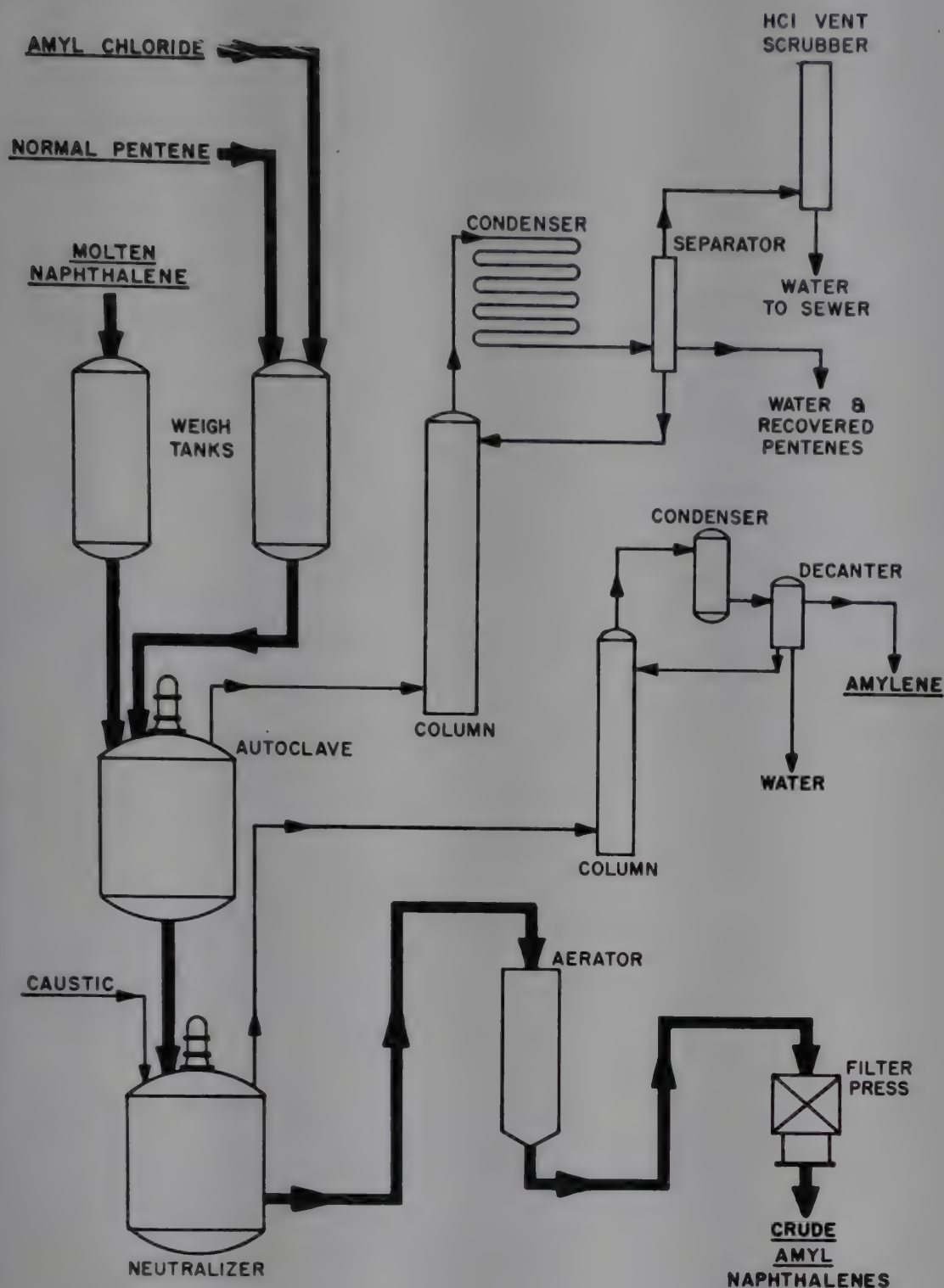


Figure 5. Flow Sheet for Production of Amyl Naphthalenes

crude mixture in the autoclave is discharged to a batch still where the hydrogen sulfide and a portion of the pentenes are distilled off. The hydrogen sulfide is absorbed in two caustic scrubbers forming sodium hydrosulfide which is used in subsequent batches. The crude amyl mercaptans are steam distilled in this still separating them from the amyl sulfides and disulfides. The residue in the still is separated into two layers; the lower aqueous layer is disposed of with no subsequent treatment and the upper sulfide layer is sent to storage. The crude amyl mercaptans are sent to a second still where the last traces of hydrogen sulfide and pentenes are removed. The charge is then azeotropically dried and the amyl mercaptans are separated from ethanol, amyl chloride, amyl alcohol, and amyl sulfides.

Control of odor is the biggest problem in this process. All vents from the scrubbers and tanks are connected to a header which leads to a flare. This flare handles all hydrogen sulfide and amyl mercaptan vapors. Aqueous discharges are chlorinated before dropping to the sewer. Chlorination converts the odorous mercaptans and sulfides to sulfoxides and sulfones. The blending room, where open streams of mercaptans are present, is ventilated by an exhaust blower which discharges through an activated charcoal tower. By constant vigilance, escaping odors from this process are kept to a minimum.

In a series of reactions involving the use or formation of such materials as chlorine, hydrochloric acid, caustic, and brine, tremendous problems of corrosion would be expected. Although these problems were almost overwhelming during the initial stages of operation, most of them have been satisfactorily worked out.

Clark (6) pointed out that the dehydration of the pentane was originally attempted in coke-packed towers. Because of the gradual disintegration of the coke and packing of the wetted coke, the towers required frequent cleaning and replacement of packing. The remedy found was the one that is still in use today—bubbling anhydrous hydrochloric acid through the pentane.

By carefully maintaining anhydrous conditions, it is possible to use carbon steel equipment for the chlorination. A carbon film forms in the Venturi mixer and undoubtedly serves as an effective protective coating.

Where the aqueous hydrochloric acid must be handled, ceramic, resin-impregnated asbestos, and rubber-lined equipment is successfully used. More expensive metals such as tantalum have been considered, but an economic balance of their high initial cost against the replacement costs of the present materials does not indicate that use of such metals would be advisable.

Corrosion in the No. 1 digester is negligible because the unit is always full of liquid. In the No. 2 digester, which is operated with a vapor chamber, the corrosion is evident. The possibility of using a different type material for construction of the upper section is being considered.

The scrubber for vented hydrogen chloride vapors is a barrel-like structure made entirely of wood and containing several perforated plates.

Corrosive conditions in the preparation of phenol derivatives are met by the use of glass-lined equipment and nickel-clad autoclaves. Stainless steel equipment is used for handling distilled amylphenols because iron would cause discoloration of the product.

Some of the important pieces of equipment along with the materials of construction are listed in Table V.

SAFETY

With large quantities of flammable, volatile, and skin-corrosive materials as well as toxic gases to contend with, attention to safety is particularly important. Safety systems and devices designed specifically for the process are found throughout the plant.

Fire prevention and fire fighting are planned in great detail. All persons entering the plant are required to surrender matches and smoking is not tolerated in any of the danger areas. Non-sparking shoes are worn by all operators in the fire hazardous areas; toe or heel plates are expressly prohibited.

Emergency steam hoses are located at convenient points throughout the plant. Immediately on spillage of any flammable material, the area is blanketed with steam to prevent fire while the material is being cleaned up. Instructions are issued to all operators pointing out the danger of throwing any electrical switch in an explosive atmosphere.

The pentane dehydration tank and the make-up tank are situated adjacent to each other in an area surrounded by a Transite wall. The door to the area is kept closed at all times, except when an operator is inside. The entire area can be flooded with live steam in event of a fire. The shed around the coal-fired pipe still can also be flooded with steam in an emergency. Valves on the steam lines to these zones are located away from potential fire areas.

Wherever necessary, all vents carrying flammable vapors are run to the outside of the buildings and are protected with flame arrestors.

All motors and other electrical equipment are of explosion-proof design when installed in any area where flammable vapors might be encountered.

The two-story building housing the digesters and the alcohol rectification units is equipped with one indoor and three outdoor slide poles for rapid exit. In addition, the second floor is connected by a walkway to an adjacent building.

A specially engineered fire alarm system (5A) is installed throughout the plant with boxes located at strategic points. Employees are instructed to turn in as an alarm any emergency which could lead to a fire.

Each storage tank for holding pentane received by tank car is surrounded by a dike about 3 feet high. A fire fighting system, controlled at a central station, is piped to each of these dikes. In the control house there is a mixing chamber which is connected with a feed line from the plant water system; foam generating chemicals are available and can be added to the water at this point.

Operators who would be able to leave their production units in an emergency are designated as members of the plant fire squad; squad members participate in special training drills.

At the first sound of the fire alarm, the plant water pressure is immediately increased by the powerhouse. When the squad member assigned to the foam generation unit is notified of a fire in one of the dike areas, he opens the valve which feeds the dike in that area and dumps into the mixing chamber a 5-gallon can of foam generating chemical. Several dikes in the adjacent areas are also flooded with foam. The entire dike system is outlined in colors on the wall of the fire control house with each dike area painted a different color and the valve which feeds that dike area painted the same color.

It is important in the Venturi mixing chamber, where pentane and chlorine are combined under pressure, that the pressures of the two components are maintained in the proper relationship. To prevent the entrance of chlorine into the pentane system, an indicator light device is attached to the pentane feed chamber. When the pressure is maintained at the proper level a green light burns, an excessive pressure rise lights an amber light, and a red light indicates a drop in the pentane pressure.

Respirators with cartridges for chlorine or hydrogen chloride vapors are provided at convenient points. Operators are required to wear a respirator when changing chlorine supply cars, and gas masks with chlorine canisters are available in case of any major leaks.

In the derivatives processes, phenol, caustic, acetic and sulfuric acids, as well as the various amyl compounds must be handled safely. Rubber gloves and goggles are required attire when operators are exposed to any of these skin-corrosive chemicals.

CONTROL

Two separate control groups are maintained at the Wyandotte plant. The regular control laboratory checks all raw materials as well as some of the materials in process and finished products.

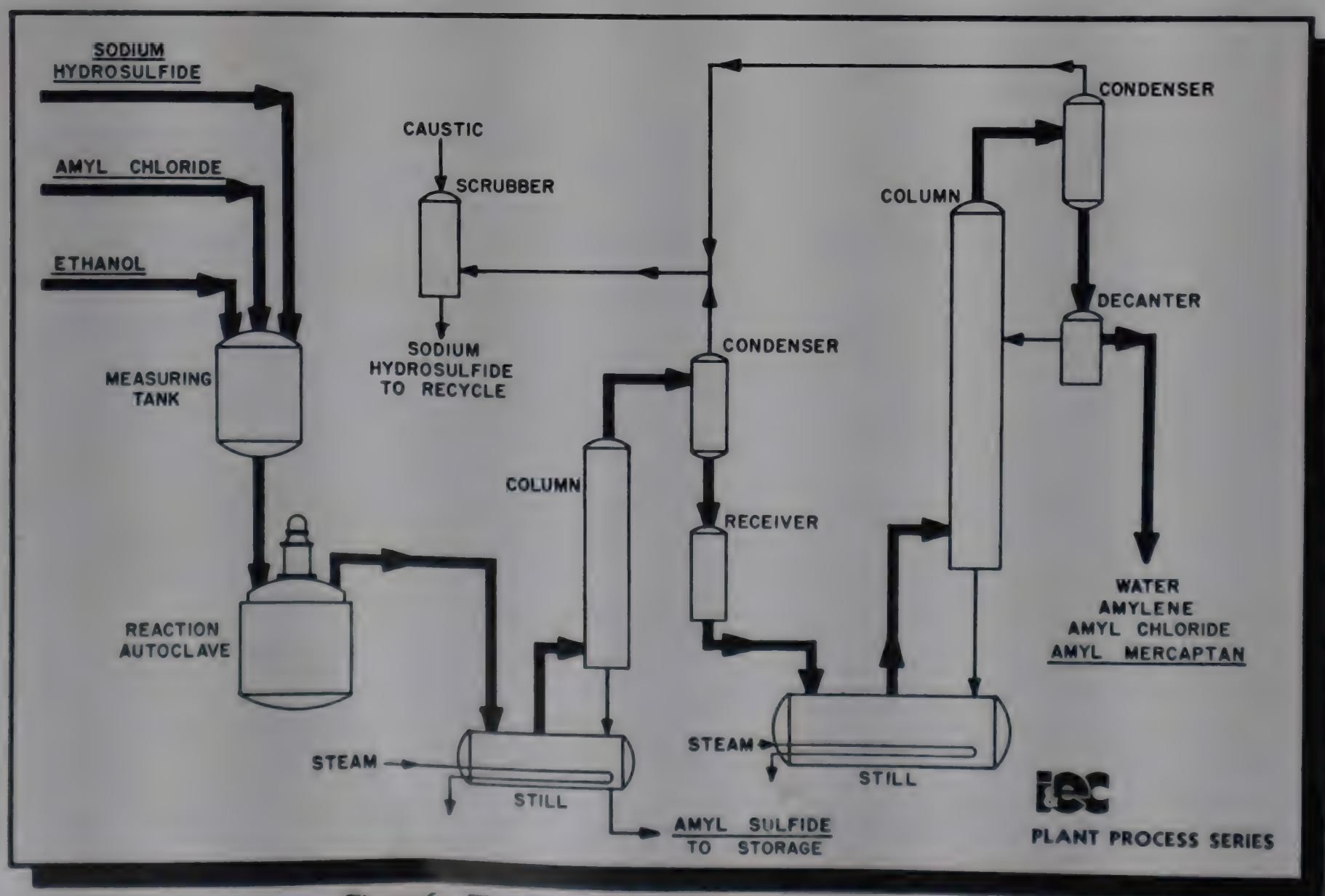


Figure 6. Flow Sheet for Production of Amyl Mercaptan

The shipping control group checks all materials prior to shipping. Although much of the routine process control testing is done by the plant operators, there are analysts in the laboratory for each shift.

Raw Materials. The boiling range is checked on samples from each car of mixed pentanes received. Initial boiling point must not be below 27° C. and 95% of the sample must boil in the range of 28° to 39° C.; final boiling point must not be above 40° C. Infrared absorption analyses are made on every car for company reference and for billing purposes.

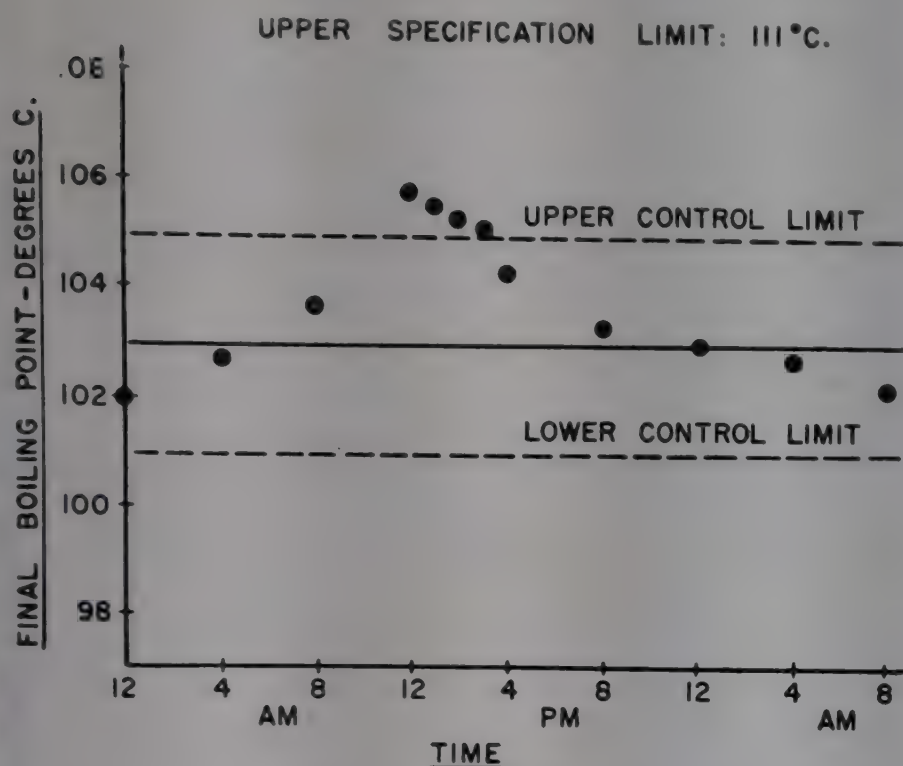


Figure 7. Sample Control Chart

It is extremely important that the water content of the chlorine be controlled; specifications require this to be less than 0.01%. Samples from each car are analyzed by a gravimetric absorption technique.

Freezing point determinations are used to check the purity of the incoming phenol, naphthalene, and acetic acid. Caustic samples are titrated for sodium hydroxide content and the iodine number is run on samples of oleic acid. However, neither specification is critical.

Process Materials. As far as is practical, all control testing is done in the plant at the site of the operation and by the operator.

Laboratory equipment used in the plant has been modified and standard solutions adjusted so that the plant techniques and calculations are relatively simple.

Control of the fractionating towers after the chlorination reaction offers a good example of the type process control encountered in the plant. The final vapor temperature of the first column is maintained at approximately 40° C. Special control is exercised in column No. 3 to keep the final boiling point of the distillate low enough to prevent distillation of dichlorides. Control charts have been set up plotting the final boiling point against time; a sample chart is shown in Figure 7. The control limits have been determined by a statistical analysis of data from several years of operation. Although the upper specification limit is 111° C., the control limit is 105° C. A sample of the distillate is taken every 4 hours. When the boiling point goes out of control, samples are taken as often as every half hour until changes in feed, reflux, or take-off correct the situation.

To make certain that all monochlorides are being distilled off, a sample is also taken from the bottom of the No. 3 column every 2 hours. Initial boiling point of this sample must be above 135° C.

The amyl chloride in the receivers from column 4 is analyzed

by specific gravity measurement each time one is full. If the specifications are not met, the product is returned to the column.

At other points in the process a statistical study of the necessary sampling frequency has been made. In several cases it was found that many more samples were being taken than were actually necessary to keep the operation running within the control limits.

Customer Complaints. All complaints from customers are reported to the control group by any employee who receives or hears of them. Investigation is made immediately to assign causes and make corrections. Record cards are kept on each product showing complaints per 1000 shipments. By means of control charts whose limits have been determined by statistical study, the quality of the production and shipping techniques can be determined at a glance.

Complaint causes are also broken down as to department or operation; this breakdown includes such classifications as procedure, operation, handling, carrier, and vendor. These data are also subject to careful statistical study and are available to top management in the form of regular reports.

ECONOMICS

The operation of the chlorination, hydrolysis, and esterification units on a 7-day continuous schedule requires a total of 28 men, each working an average of 42 hours per week. For the production of amylphenols, mercaptans, and naphthalenes an additional 28 operators are required.

Four shift superintendents working under an operations manager provide night and week-end supervision for the plant. The entire plant is divided into three areas, each with its own day supervisor. These area supervisors work only days but are on 24-hour emergency call. The shift superintendents are selected on the basis of their previous operating and supervisory experience; all have worked as operators themselves.

The cost distribution in the production of the chloride, alcohol, and acetate is presented in Table VI. The value of the by-products is treated as a credit to the cost of raw materials, and starting materials which are produced at the plant are charged at factory cost.

TABLE VI. COST DISTRIBUTION
(Cents per dollar of total cost)

	Cost		
	Amyl chloride	Amyl alcohol	Amyl acetate
Raw material cost less by-product credit	67	78 ^a	91 ^a
Direct labor and supplies	20	12	4
Indirect labor and supplies	13	10	5

^a Includes starting amyl compound at factory cost.

The direct labor and supplies include utility costs, operating labor, maintenance labor and materials, and miscellaneous process supplies. Charges for indirect labor and supplies cover such things as materials handling, control, shipping, and billing.

Utility requirements for an average day of operation are summarized in Table VII.

An indication of the amount of recycled material as well as the total raw material requirements is given in Table VIII.

TABLE VII. UTILITIES REQUIREMENTS
(Per day of operation)

	Amyl Chloride	Amyl Alcohol	Amyl Acetate
Steam, thous. lb.	450	440	115
Water, thous. gal.	1000	700	540
Electricity, kw.-hr.	700	45	130
Coal, tons	3.5



Batch Still for Alcohol Distillation

TABLE VIII. RAW MATERIAL REQUIREMENTS

(For 10,000 pounds of product)

	Product		
	Amyl chloride	Amyl alcohol	Amyl acetate
Raw materials consumed, lb.	15,500	27,500	12,000
Raw materials processed, lb.	Not available	60,000	16,000

FUTURE PROSPECTS

The isomeric amyl alcohols are finding increased use in lubricants, plasticizers, pharmaceuticals, and chemical syntheses where a particular molecular configuration or chemical property is required. The mixed amyl alcohols offer the best source of these isomeric amyl alcohols and the prospects are that these uses will grow. The market for mixed isomers has changed very little in the years it has been available. No essential change in the uses of amyl acetate can be discerned, nor are there any new defi-

nite trends apparent relating to the future of the other amyl derivatives described.

Should the market for the amyl compounds expand, there have been fundamental plans laid for a duplication of the present installation for chlorination and hydrolysis. Further instrumentation and a few changes in materials of construction might be expected in any expansion, but the basic process would be the same.

The fact that Sharples has been able to operate with a reasonable profit and with few changes in basic design for so many years may be an indication of what the future holds for others entering the chemicals from petroleum field.

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- (10) Sharples Chemicals, Inc., Philadelphia, Pa., "Synthetic Organic Chemicals," 15th ed., p. 7, 1947.
- (11) *Ibid.*, p. 15.
- (12) *Ibid.*, p. 47.
- (13) *Ibid.*, p. 51.
- (14) *Ibid.*, p. 58.

PROCESSING EQUIPMENT

- (1A) Dow Chemical Co., Midland, Mich., heat transfer medium, Dowtherm.
- (2A) Fairbanks, Morse & Co., Chicago, Ill., railroad track scales.
- (3A) Fisher Governor Co., Marshalltown, Iowa, liquid-level controllers and traps.
- (4A) Foxboro Co., Foxboro, Mass., liquid-feed controllers.
- (5A) Gamewell Co., Newton Upper Falls, Mass., fire alarm systems.
- (6A) Haveg Corp., West Newark, Del., acid-resistant chemical equipment.
- (7A) Iron Fireman Mfg. Co., Portland, Ore., automatic coal burners.
- (8A) Pfaunder Co., Rochester, N. Y., glass-lined equipment.
- (9A) Thermal Syndicate, Ltd., New York, N. Y., *Bull.*, **4**, Vitreosil gas absorbers.
- (10A) Wallace and Tiernan, Newark, N. J., high-capacity chlorine flowmeter.

Phenol by Sulfonation

RICHARD L. KENYON

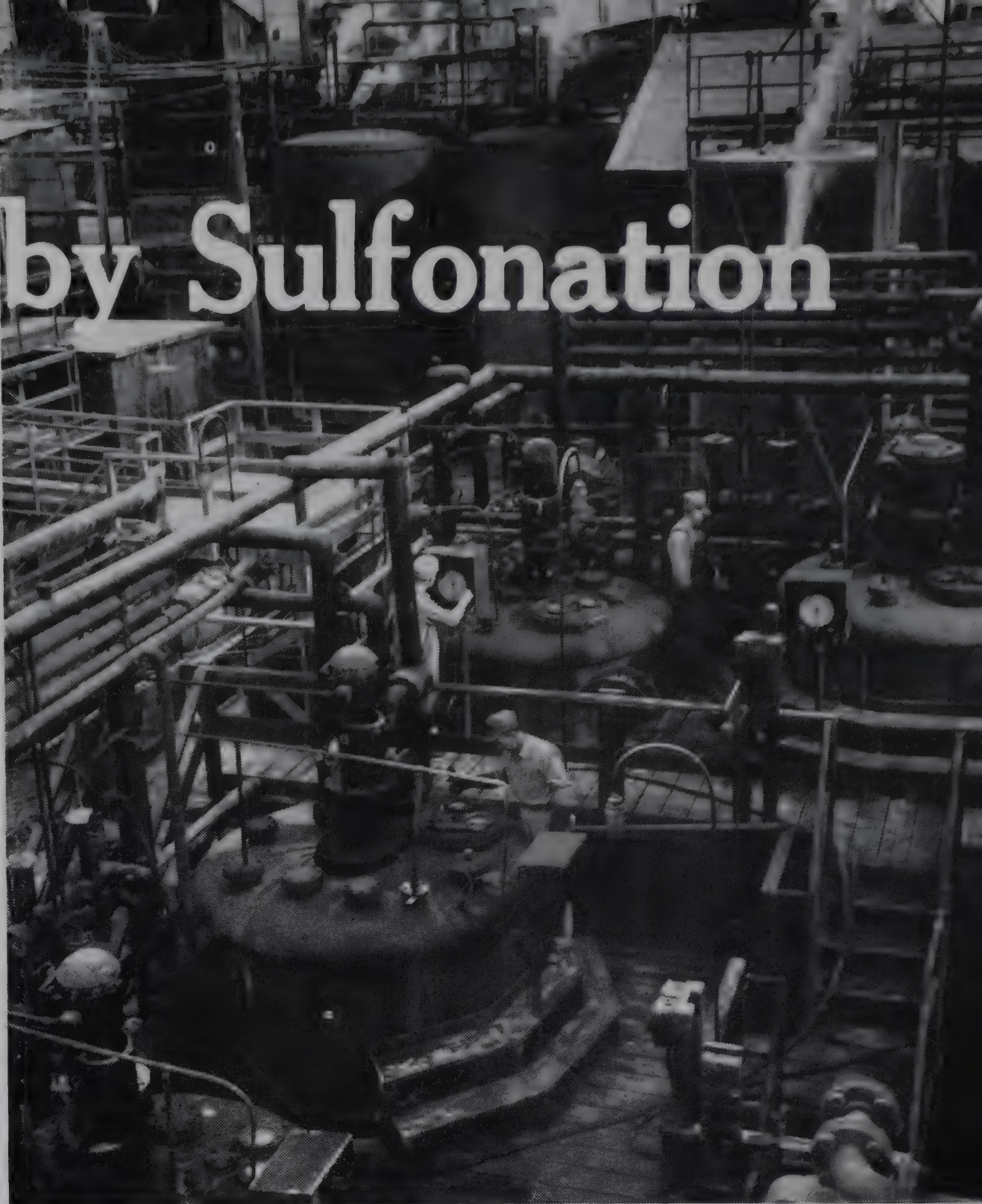
Associate Editor

in collaboration with

N. BOEHMER

*Monsanto Chemical Company,
St. Louis, Mo.*

**Sulfonation System, Monsanto, Ill.,
Phenol Plant**



THE history of phenol production in the United States has been one of great fluctuation, affected particularly by wars. There have been rapid shifts from excess supply to shortage, with extensive effect on the industry, as can be seen from tracing the history of this segment of the chemical industry.

Phenol was first discovered by Runge, in 1834, when he isolated it from coal tar. It remained a natural product for nearly a half century until Wichelhaus realized the value of the reaction, discovered in 1826 by Faraday, by which aromatic sulfonic acids could be fused with alkali to yield the hydroxy compounds. This was applied primarily to the preparation of β -naphthol, important in the dye industry, when it was first brought into commercial use, but during the 1890's synthetic phenol was made in Germany, in insignificant quantities, by the alkali fusion of benzenesulfonic acid.

During the Boer War, England placed an embargo on phenol, which caused a shortage on the continent. As a result, the F. Raschig works, at Ludwigshafen, Germany, went into the manufacture of the synthetic product on a large scale. Hoffmann-LaRoche, Basle, Switzerland, also began producing about this time, mostly for the pharmaceutical industry.

In 1913 the only production in the United States was of the natural product from coal tar, by the Barrett Manufacturing

Company, now the Barrett Division of the Allied Chemical and Dye Corporation. Medical uses represented the greatest consumption, although the new phenol-formaldehyde resins and a few chemical compounds in commercial production used phenol as a starting material. Prewar consumption of phenol was about 5,000,000 pounds per year (24). Thomas Edison had built a plant which was producing synthetic phenol for the manufacture of phonograph records, but no others were operating at the outbreak of the war.

The supply of picric acid and dyes was cut off with the beginning of World War I, throwing this country on its own resources with the result that production sprang up rapidly. By 1915, Barrett was making the synthetic product in its Frankford, Pa., plant. Solvay Process Company, at Syracuse, N. Y., and Dow Chemical Company entered the field in that same year. In the following year, Monsanto Chemical Company, Milwaukee Coke and Gas Company, and the Commercial Acid Company became active in phenol manufacture. The last company was acquired by Monsanto in 1917. The largest unit, with a designed capacity of 35,000,000 pounds per year, was begun by Barrett but remained unfinished because of the end of the war. Consumption had reached 72,000,000 pounds per year at the time the United States entered the war (24).

When hostilities ended there was on hand a large government supply and no demand. Plants were dismantled, and the industry seemed to have fallen apart. But by 1922 the picture had changed again: because of the growth of the manufacture of phenol-formaldehyde resins, the surplus of phenol had disappeared. Heyden Chemical Company began producing the next year. Monsanto constructed a plant at Monsanto, Ill., which went into operation in 1923. Dow installed the process for the manufacture of phenol from chlorobenzene in 1924 (2), and the Bakelite Company began producing at Painesville, Ohio, continuing until 1928 (28).

By 1938, almost all the synthetic phenol production in the United States was operated by Dow and Monsanto (28); the total capacity was near 90,000,000 pounds. In 1940 Durez Plastics and Chemicals, Inc., began operating its new 15,000,000-pound-per-year plant (1) employing the Raschig, or regenerative, process, and Barrett put a sulfonation process plant into operation. The war stimulated production once again. The Catalin Corporation installed a small unit in 1942, which is no longer operating. Reichhold Chemical Company's sulfonation process unit in Tuscaloosa, Ala., went into operation late in 1943 (29). The Solvay plant produced for a few months in 1943-44. General Electric built a plant at Pittsfield, Mass., which began production by caustic treatment of chlorobenzene in 1946, and Heyden acquired an ordnance plant in Memphis, Tenn., in that year, with the intention of manufacturing phenol but never made phenol in that plant.

Once again the end of hostilities left an excess of phenol production capacity, but within a few months its use in the manufacture of a number of products passed the demand and expansion was resumed. In 1947, capacity was increased by 42,000,000 pounds to a total of 300,000,000. Nobell Resins Company, Azusa, Calif., built a sulfonation process plant of 3,000,000-pound capacity in 1948, when they could not procure phenol on the West Coast. It went into operation in January 1949, but closed after 2 months because of the market price at which phenol be-

TABLE I. NATURAL AND SYNTHETIC PHENOL—NEW SUPPLY AND EXPORTS¹

	New Supply, Net	(In thousands of pounds)			Imports ^b	Exports ^c
		Total ^b	Synthetic	Natural		
1913	9,346 ^d	1,000 ^d	0	1,000 ^d	8,346	...
1914	11,383 ^d	3,000 ^d	2,000 ^d	1,000 ^a	8,393	...
1915					3,106	
1918	100,599	106,794	100,000 ^d	7,000	283	6,478
1922	1,559	1,286	0	1,286	496	223
1923	3,208	3,311	1,300 ^e	2,000 ^b	130	233
1924	11,021	10,522	8,000 ^e	2,500 ^b	550	51
1925	15,089	14,734	12,000 ^e	2,700 ^b	355	...
1926	8,935	8,691	7,000 ^e	1,700 ^b	244	...
1927	8,654	8,041	6,000 ^e	2,000 ^b	613	...
1928	11,205	10,227	8,200 ^e	2,000 ^b	978	...
1936	47,537	48,724	36,700 ^f	12,000 ^e	71	1,258
1937	65,722	65,690	50,900 ^f	14,800 ^e	32	...
1938	44,548	44,548	30,750 ^f	13,800 ^e
1939	66,519	68,577	53,000 ^f	15,600 ^e	...	2,058
1940	91,851	96,155	72,188	23,968	...	4,304
1941	111,861	115,047	92,922	22,125	...	3,186
1942	127,016	146,125	127,632	18,493	...	19,109
1943	164,129	194,967	181,347	13,620	...	30,838
1944	178,686	201,993	173,141	28,852	...	23,307
1945	188,280	205,112	181,640	23,472	...	16,852
1946	179,143	203,829	183,855	19,974	...	24,686
1947	247,913	268,460	245,000 ^e	23,500 ^e	1	20,558
1948	267,280	297,338 ^g	274,274	23,064	...	30,058
1949	201,602	224,544 ^g	207,969	16,175	...	22,942

^a Dyes & Synthetic Chemicals; U. S. Tariff Commission, 1918-46; 1947 preliminary. ^b Foreign Commerce & Navigation; all grades of phenol—i.e., 30%; data obtained from analyses in various tariff reports; see also Phenol, Tariff Commission, 1928; 1936-40 Commerce Statement 3865. ^c Foreign Commerce & Navigation; 1918-26, Phenol, Tariff Commission, 1928; 1913-37, Report No. 131, 2d series, p. 15, Tariff Commission. ^d Approximate only. ^e Approximate and based upon statements made in annual tariff reports and the trade. ^f Approximate; natural phenol estimated from quantity of tar distilled and synthetic phenol estimated by difference.

^g Data and footnotes through 1947 reproduced from Chem. Eng. News (28).

^h U. S. Tariff Commission, Syn. Org. Chemicals, Rept. 164, 2nd series.

TABLE II. SYNTHETIC PHENOL—CAPACITY AND PRICE¹

	(In millions of pounds)			Producers ^d Number, Active	Price, U.S.P.
	As Rated ^a	Inopera- tive ^b	Net ^c		
1913	0	0	\$0.113
1914	3 ^e	1	0.203
1915	90 ^e	5	1.271
1918	100 ^e	6	0.53-0.30
1922	5 ^e	0	0.176
1923	10 ^e	4	0.37
1924	20 ^e	6	0.28
1925	20 ^e	6	0.224
1926	20 ^e	6	0.197
1927	20 ^e	5	0.169
1928	14 ^e	4	0.15
1938	90	0	90	2	0.145
1939	90	0	90	2	0.138
1940	118	0	118	4	0.129
1941	118	0	118	4	0.123
1942	154.5	0	154.5	5	0.125
1943	250.5	30	220.5	7	0.106
1944	255	30	225	6	0.105
1945	255	30	225	6	0.105
1946	258	30	228	6	0.106
1947	300	30	270	6	0.114
1948	280 ^h	5	275	6	0.12
1949	340 ^h	132	208	7	0.125
1950	410 ^h	160	250 ^h	6	0.155

^a 1938-, as developed from announcements and communications; rated signifies expected and as engineered to obtain whether operative or not. ^b Rated capacity less than shown to be obtainable subsequently; does not include capacity inoperative because of benzene shortage; the Memphis, Solvay, and GE plants make up the totals. ^c Realizable capacity (see ^b); includes the GE plant to the capacity, obtained. ^d Producers operating "net capacity"; this excludes the Memphis plant 1943-48; excludes the Solvay plant all years. ^e Approximate only; trade estimations are various, both higher and lower than cited here.

^f Data and footnotes through 1947 reproduced from Chem. Eng. News (28).

^g Based on published figures and private communications. Memphis and Solvay plants excluded; year-end estimate, 1950.

^h Based on extrapolation from U. S. production figures for first quarter.

came available. Since that time no new companies have entered the field, although some have expanded plant capacities. Bakelite has indicated plans to open a plant employing the regenerative process in Marietta, Ohio, probably late in 1950.

At the present time Dow and Monsanto are the leading producers. Others contributing significant quantities include Barrett, Reichhold, and Durez.

TABLE III. PHENOL CONSUMPTION

(Distribution of consumption in the United States^a, 1944, exclusive of military requirements)

	%
Phenolic resins and adhesives	66.0
Manufacture of chemicals	7.2
Medicinals, including salicylates	8.1
Petroleum chemicals and petroleum refining	6.6
Disinfectants and insecticides	3.6
Plasticizers	2.8
Toluene extraction	2.7
Dyes and inks	1.5
Miscellaneous uses and small orders	1.5

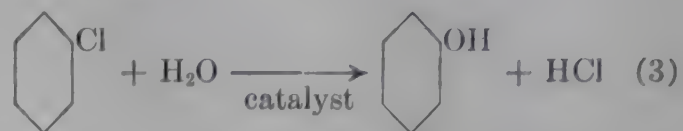
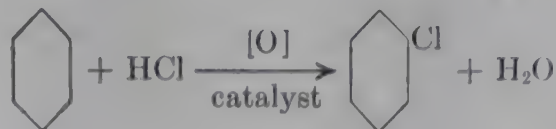
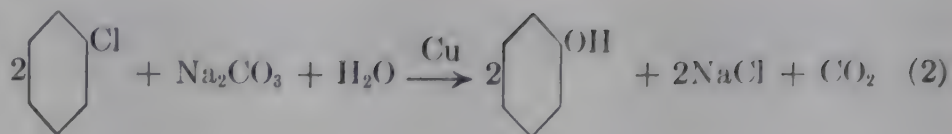
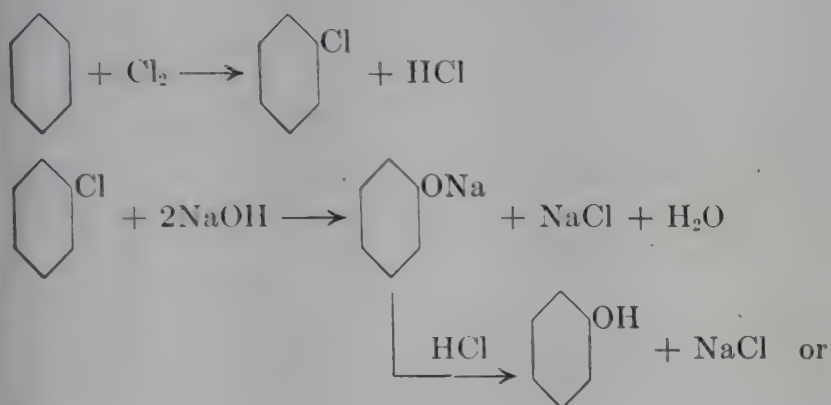
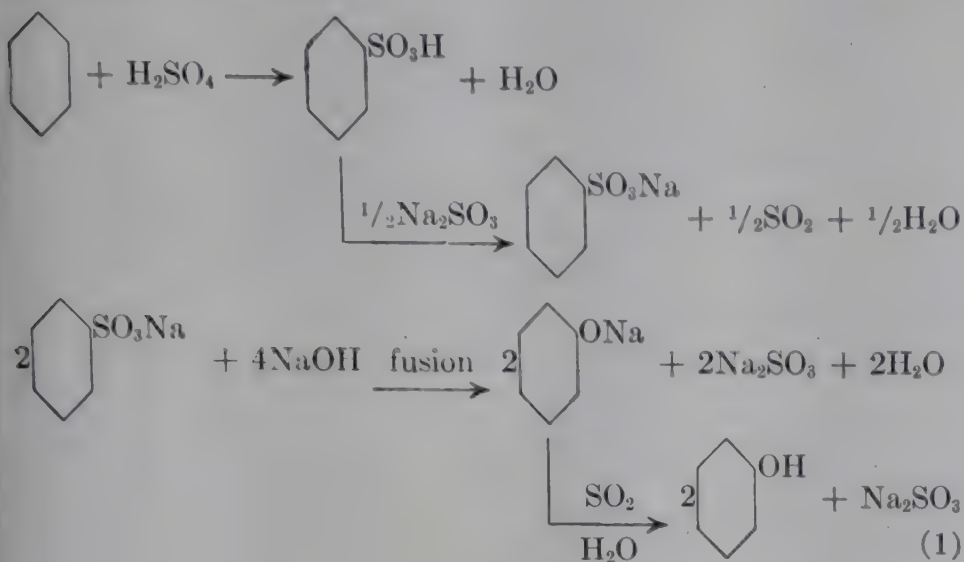
^a Data from information issued by U. S. Department of Commerce on allocations of phenol.

The mushroom growth following World War II was accounted for partly by foreign demand, but other major factors included growth of the plastics industry, waterproof plywood production, and the use of phenol in petroleum refining. The development of the use of pentachlorophenol for wood-treating, slime and algae suppression, and tanning and the discovery of the weed-killing properties of 2,4-dichlorophenoxyacetic acid were major contributing factors.

FUNDAMENTAL CHEMISTRY AND COMMERCIAL PROCESSES

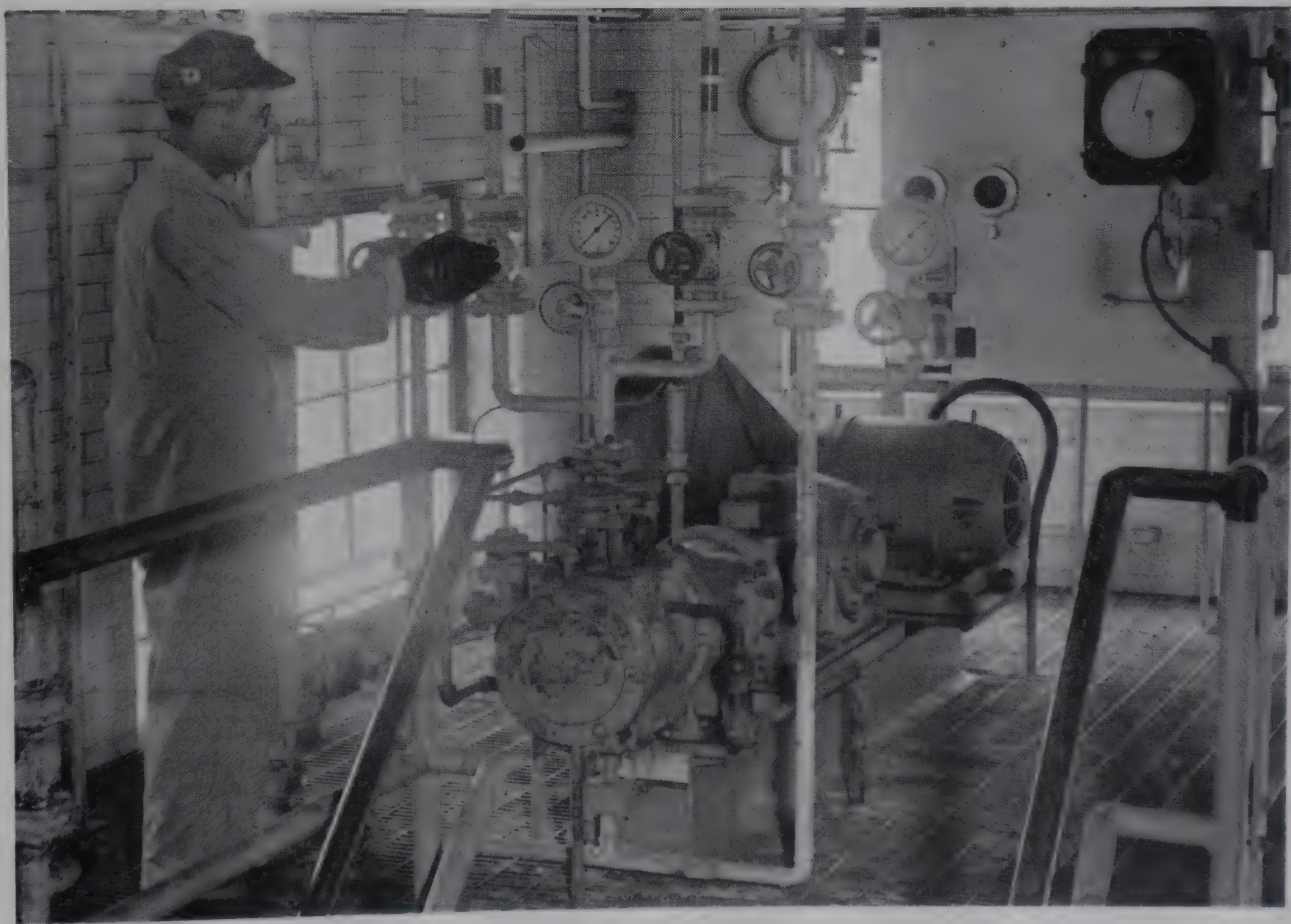
Phenol can be prepared by means of any of a number of organic chemical reactions. Considerable attention has been given to the manufacture of phenol by the direct oxidation of benzene with air, using a great variety of metallic catalysts (31) iodine (17), and oxides of nitrogen (5, 6), as well as noncatalytic processes

(7, 20, 21). The inclusion of small amounts of organic materials of diverse types has been found to improve the reaction (11, 18). However, only three methods have been put into commercial application. They are:

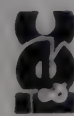


Of these reactions, Process 1 is the oldest; it is the process used by Monsanto and the subject of this article. The old process used 100% sulfuric acid; the excess was later neutralized. A major problem existed in the dilution of the sulfuric acid by water produced in the reaction. The Tyrer process (30) improved on this process by passing benzene vapor through sulfuric acid at concentrations as low as 90% and temperatures varying from 100° to 185° C. The unreacted benzene carried out water, keeping the sulfuric acid concentration constant. Similar processes were developed by Barbet (4) and Guyot (13).

Dennis (10) found that benzene would take up 2 to 3% of its own volume of benzenesulfonic acid, and Bull (8) developed a process which saved 90% of the excess sulfuric acid as spent acid of a concentration of 70 to 77%. This became the Dennis-Bull process in which sulfonation and extraction were carried out in one operation, the sulfonic acid was removed from the benzene with water, the aqueous solution was evaporated to remove benzene, and the resulting product was neutralized. The phenolate was neutralized with carbon dioxide instead of sulfuric acid.



Sulfur Dioxide Compressor



PLANT PROCESS SERIES

Figure 1. Flow Sheet for Manufacture of Phenol at the Monsanto, Ill., Plant of Monsanto Chemical Company



Fusion Pot Operation Platform

Process 2 was first applied by the Dow Chemical Company to make phenol in 1924. The process was originally patented by Aylsworth (3), and Dow was granted a license. The original Aylsworth process did not succeed because of the accumulation of diphenyl ether which, at that time, was a useless by-product. The Dow process overcame this difficulty by returning the diphenyl ether to the reaction mixture, forming an equilibrium mixture and preventing the formation of more of the ether (14). The situation has been made more favorable since the first development of the process by the use of diphenyl ether as a component of heat transfer media, Dowtherms, now in wide use. This process can be operated (12, 15, 16) using the reaction of sodium carbonate with chlorobenzene in copper vessels to obtain phenol directly without additional acid treatment. In 1915, a statement was published (22) to the effect that because of the high temperatures and dilute solutions of caustic required to convert chlorobenzene, the process was not favorable. "For this reason," it was stated, "which necessitates the use of autoclaves for very high pressure and large volume, the industrial application of this elegant short method for preparing synthetic phenol is out of the question."

The Dow process now consists of treating chlorobenzene with aqueous caustic solution in an iron tubular autoclave system at temperatures of about 350° to 360° C. The reaction mixture from the autoclave system is allowed to settle and from the non-aqueous layer is derived diphenyl ether which is returned to the process. The alkaline aqueous layer is acidified and from the liberated phenolic layer are obtained phenol, *o*-phenylphenol, and *p*-phenylphenol.

The General Electric Company plant, which employs caustic treatment of the chlorobenzene, has been described (19). Caustic solution (10 to 15%) is mixed with monochlorobenzene in a mole ratio of 2 to 2.5:1, diphenyl ether is added, and the mixture is heated to about 370° C. at a pressure of about 4000 pounds per square inch. The product is neutralized with hydrochloric acid to obtain phenol.

Process 3 was developed in Germany under the direction of Prahl, for the Raschig Company (26, 27), in the search for a phenol process with a smaller proportion of by-products (9). By finding a catalyst which could be used economically to effect

the hydrolysis of chlorobenzene by water and learning how to oxidize the chlorine from the recovered hydrochloric acid in the presence of benzene to yield monochlorobenzene, he succeeded. The process, in its net effect, amounted to the direct oxidation of benzene. This process was brought to the United States by Durez Plastics and Chemicals, Inc., and by 1940 that company was producing phenol with it. Dichlorobenzenes are produced in the chlorination stage and polydiphenyls result in the hydrolysis in the respective amounts of 6% and 2% of the U.S.P. phenol output, it is reported (9). This process has been described in some detail (12, 23).

MONSANTO'S PHENOL OPERATIONS

The Monsanto Chemical Company began the operation of a small synthetic phenol plant in St. Louis in 1916. At about the same time, the Commercial Acid Company started producing phenol by the benzenesulfonate fusion process in what is now Monsanto, Ill. That plant was purchased by Monsanto in 1917 and continued in operation along with the other until early in 1919. Monsanto had purchased a large quantity of the United States Government's surplus stock at the end of the war and there was no need for manufacturing more at that time. Both plants were almost completely dismantled with the idea that an improved process would be used when the manufacture of phenol was resumed.

In 1923 phenol production was resumed by Monsanto. By this time they were producing both caustic soda and sulfuric acid in Monsanto, Ill., and as a result the plant was located there. A department with a capacity of 3,000,000 pounds per year was established, using the same basic operations as did the old process, combining new developments with the best features of both the previous plants. The new plant employed two 6-foot diameter fusion pots. As progress was made, another pot was installed and production was increased by about 50%. In 1929 the equipment then in use was moved to the present location, and additional equipment was installed to bring the over-all capacity of the plant up to about 12,000,000 pounds per year. In 1934 this was again increased, by 25%, by the installation of additional equipment. Since that time, capacity has been increased about fivefold. This has been accomplished through conversion to an almost continuous process plus other refinements and improved methods of operation.

Economic Considerations. It has been indicated that the supply-demand situation in phenol has not been regular or consistent during its history. This poses the question of economic practicability of its manufacture over a period of time. One answer to this problem is the manufacture of products based on phenol, for which a reasonably dependable market can be developed. Enough of these products to reduce the likelihood of a weak demand in all at the same time, under sound general economic conditions, gives stability to the situation.

Monsanto uses its own phenol to manufacture pharmaceuticals, such as aspirin and salicylic acid; agricultural chemicals, such as 2,4-dichlorophenoxyacetic acid; plastics, including phenol-formaldehyde polymers; chemicals for the petroleum industry; sulfonated phenols for the plating industry; and chlorinated phenols, used in wood preservatives and many other applications.

With three commercial processes developed and in use, the basis of choice of any given process deserved attention. As was stated, Monsanto had given consideration to the use of another

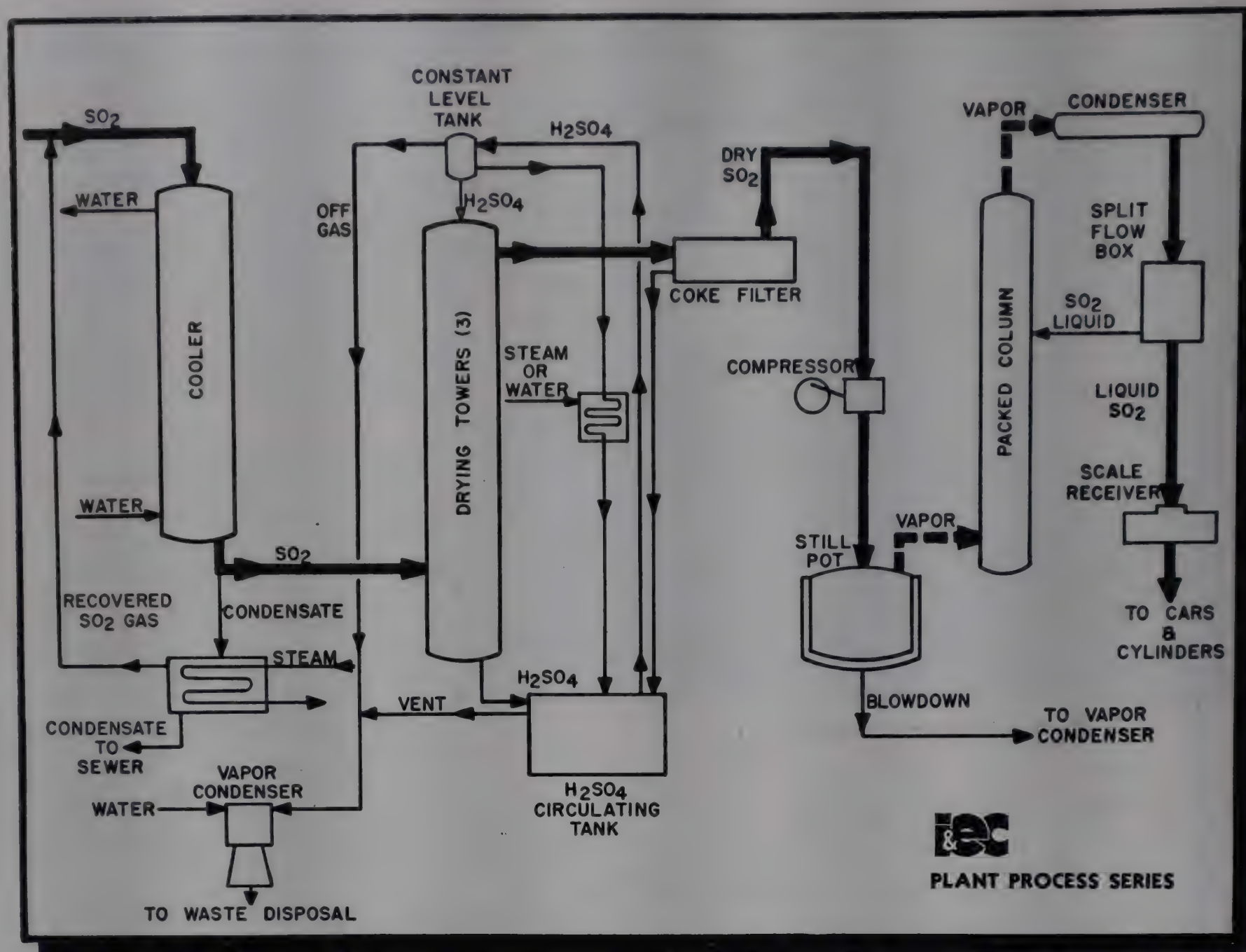


Figure 2. Flow Sheet for Recovery of By-product Sulfur Dioxide

process in reorganizing its phenol operations between 1919 and 1923.

The manufacture of starting materials by the company, on the same site as that of the phenol plant, is an important factor. Having a caustic-chlorine plant for the manufacture of chlorine as a starting material for other company products gave an ample supply of caustic. Monsanto also manufactures sulfuric acid in appreciable quantities, ensuring a constant supply at minimum cost of transfer.

In 1923, other processes which are now in commercial use had not been developed to that state of practicability. Monsanto had experience in the manufacture of phenol by the sulfonation process and was in a much better position to use it than any other process. As has been shown, improvements were made and the plant was expanded. The change to any other process would involve great expense in the loss of these developments. Consideration has been given to plant costs for another process, and it is estimated that it would cost about as much to build a new plant for another process as it would to build a sulfonation process plant of the same size. It is estimated that the cost of a

new plant for the present process, equivalent in capacity to that now in operation, would be at least \$4,500,000. Pope (25) estimated, in 1916, that to build a 10,000-pound-per-day plant would cost \$200,000; the cost for twice that capacity was set at \$250,000.

MONSANTO, ILL., PLANT

Raw Materials. Benzene is brought into the plant in steel tank cars, which are fitted with steam heating coils. It is unloaded to storage tanks by pumps driven by explosion-proof motors (2E). Standard precautions for handling flammable liquids are observed. The tanks, of capacities varying from 10,000 to 300,000 gallons are, with one exception, underground and are equipped with flame arrestors on all vents. Sulfuric acid is piped directly from the adjacent Monsanto plant. Some reserve storage is maintained to take care of unforeseen shut off of supply.

The sodium hydroxide used is also manufactured by Monsanto. It is piped from an adjacent plant and stored as 70% caustic solution in outdoor steel tanks.

Sulfonation. Benzene is sulfonated in the first step of the manufacturing process (Figure 1). This is accomplished in a continuous operation in a cascade series of six units. These units are dished-bottomed, 2000-gallon, cast-iron reaction vessels having steel agitator shafts fitted with three-bladed propellers plus cross-bar agitators. The first of the sulfonators is fitted with a cooling jacket, through which water is circulated, and also a water-cooled external shell-and-tube heat exchanger circuit. The

TABLE IV. POWER AND WATER REQUIREMENTS

Production of 100 lb. phenol and by-products

Steam, lb.	850
Electricity, kw.-hr.	11.5
Process water, gal.	125
Cooling water, gal.	1000



Acidification Tank and Tower

Phenate solution is pumped to top of tower, upper right, through vertical pipe, left center; after falling as spray and absorbing sulfur dioxide, solution returns to tank, lower left, through pipes leading from lower end of tower

second unit has cooling coils and a cooling jacket. The third and subsequent units have steam jackets for the application of heat.

Both benzene and oleum are constantly circulated through overhead wrought-iron pipe lines with drawoff connections to the reactors. Recording flow controllers are used here, and the feed is regulated in a proportion which will allow satisfactory control of the initial reaction in the first unit. The rate of feed controls the rate at which the reaction mixture flows from one unit to the next, and the temperature is set at a level which will give optimum operating conditions in each unit and will ensure completion of the reaction.

Neutralization. The sulfonated product is fed into a neutralizer system. This system consists of preliminary neutralization tanks, each of approximately 5000-gallon capacity; these are connected by valves to a line in which the sulfonation product circulates from storage. The tanks are of steel with lead lining and acidproof brick inner lining. They are agitated by means of cross-blade stirrers.

The agitators have three single cross blades at intervals on the shaft; the bottom blade is not rigidly attached to the shaft but is attached to the top blade by means of two heavy bronze chains attached near the blade ends. Thus it is able to move up and down on the shaft. If agitation is stopped, solids settle out, making a nearly solid sludge. When agitation is resumed, the bottom blade is pulled out of the sludge by the chains and in turning cuts its way down to effect stirring of the sludge back into the slurry.

The agitator blades and shaft are made of Tobin bronze, and the shaft is coated with lead in areas which are exposed to hot vapors. The units are equipped with low pressure safety seals with a head of about 18 inches of water for protection against excessive rate of evolution of sulfur dioxide.

Sodium sulfite slurry is fed into the neutralization tank at an arbitrary constant rate whereas the flow of benzenesulfonic acid solution is regulated to keep the reacting materials distinctly acid. Sulfur dioxide is produced by the reaction and is piped off through Haveg pipes, partially for use in acidification later in the process and partially to another plant for purification and liquefaction, to be sold as liquid sulfur dioxide.

The neutralized slurry is transferred to another lead and brick-lined tank called a steamer tank. Here the slurry is agitated with a paddle-type agitator, while steam is blown in to remove the remaining sulfur dioxide. The sulfur dioxide from this tank carries too much water to be practically useful and is discarded to the obnoxious vapor condenser, which is a water siphon absorber.

The residual slurry of sodium sulfate, sodium benzene-sulfonate, and possibly some acid is pumped by means of an Everdur centrifugal pump to the final adjusting tank, where sodium hydroxide solution is added to make the slurry alkaline. Although it is not necessary that these final adjusting tanks be lined, their construction is similar to that of the neutralizing tanks in order to furnish standby capacity.

The main product is now a slurry of sodium sulfate in aqueous sodium benzenesulfonate solution. It is pumped by cast-iron centrifugal pumps to steel agitated tanks from which it is fed to the centrifuge system. Centrifugation is accomplished by a battery of three solid-bowl continuous centrifuges. The first two effect the major separation of sulfate from the solution. The separated sulfate, slurried with a small quantity of water as a wash, is passed through the third centrifuge. The solution from the first two centrifuges goes to the evaporators; solution from the third is sent to the sulfite mixer to make up the sulfite slurry used in neutralization. The washed sulfate from the third centrifuge is kiln-dried for sale. The drying operation is carried out in a brick-lined, oil-fired rotary kiln. The product is shipped in bulk.

Evaporation. The solution of benzenesulfonate (NaBS) which comes from the first two centrifuges is pumped to steel storage tanks. From storage the solution goes to the evaporators. Standard cone-bottomed evaporators with external heaters are used. The solution enters the body of the evaporator then circulates through a system of three tubular heat exchangers and back to the body. The exchangers are two-pass, multitube, steam heated units, each connected with a separate centrifugal circulatory pump. Vapors from the evaporators pass through a scrubbing tower (3E) with a countercurrent flow of 25% aqueous caustic in order to remove any phenol which might have been formed and carried out. The drawoff from the bottom of the evaporator is pumped to a cone separator, where most of the sulfate is drawn off continuously from the bottom of the separator, by means of a centrifugal pump, and is returned to the tanks feeding the NaBS-sulfate slurry to the centrifuges. The concentrated solution overflows from the separator to storage, where the small amount of sulfate remaining is removed by further settling and is intermittently pumped away.

Fusion. Specially fabricated cast-iron pots are used in carrying out the fusion. These pots have vertical sides with dished-up bottoms which cause flattening rather than elongation at the temperature of operation. The agitators are of the anchor type, made of special cast alloy steel. The pots are set in brick, with the tops flush with the level of the operating platform. A dam, or rim, is built up about 3 inches around the top of the pot in order to handle any material which may accidentally boil over. Each pot is directly fired by six burners which can be operated with either natural gas or oil, thus safeguarding against limited fuel supply.

Sodium hydroxide is pumped by a nickel centrifugal pump through nickel pipe lines from the caustic plant as a 70% caustic soda solution. It is stored in a steam heated, insulated tank near the fusion pots, where it is held in a molten state. In preparation for fusion, a measured amount of caustic is run into a fusion pot and evaporated, without agitation, nearly to dryness, as indicated by a sharp increase in temperature near 300° C. Agitation of the molten caustic is then started and feeding of the NaBS solution is begun. The NaBS solution is pumped from a steel measuring tank to the fusion pot at a metered rate by means of a centrifugal pump. The rate of feed is regulated so as to maintain the fusion mass in a molten state. Most of the reaction takes place as the NaBS solution is fed in, but additional heating is required, after all the solution has been added, to drive the reaction to completion.

When the fusion is completed, the material is drained through a side nozzle in the pot which is closed with a plug valve. To this plug valve is attached a nipple closed with a cap. In tapping out a batch, the cap is first removed, then the plug valve is opened. Usually, some of the fusion mass solidifies in the outlet nozzle

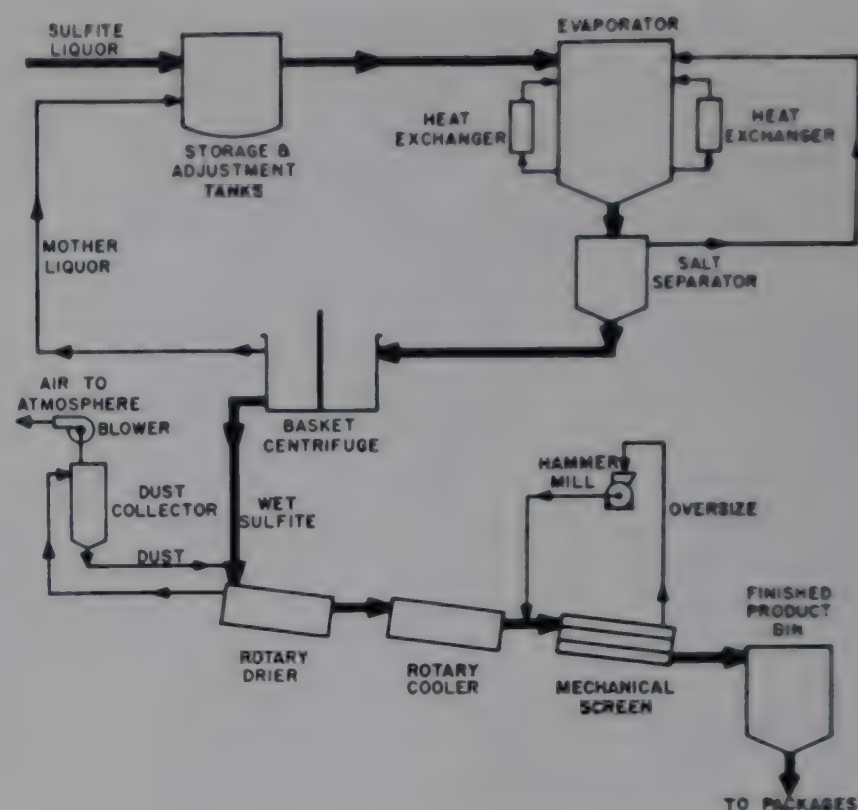


Figure 3. Flow Sheet for Recovery of By-product Sodium Sulfite

behind the plug valve and must be washed to the quencher before the batch will flow out.

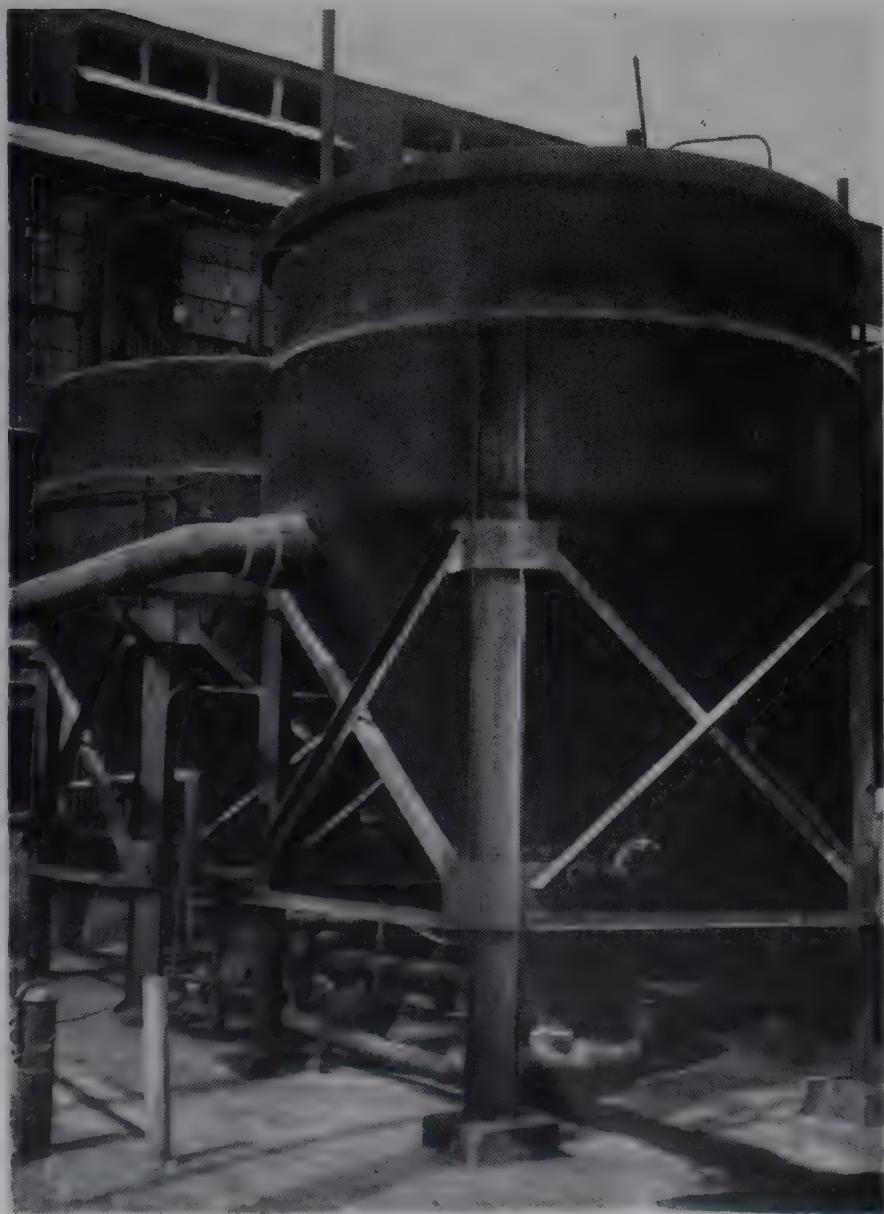
The quenching operation consists of running the fusion mass into an agitated tank containing a weak solution of sodium phenate, which is the wash water from the washing of sulfite filtered from the quenched fusion slurry. No cooling or heating is necessary and the steam generated passes out the stacks, which are equipped with separators to collect entrained material and return it to the quencher. The resulting slurry of sodium sulfite and sodium phenate is run to automatic, successive batch centrifugal separators. These separators (1E) consist, fundamentally, of a basket on a horizontal shaft. Slurry is fed inside the basket until it is filled with solid. The cake is washed once with water, after which the machine automatically digs it out.

The solid separated in centrifugation is sodium sulfite and is used in the earlier neutralization. The centrifugate, which is sodium phenate solution, goes next to acidification. The wash water is used for future quench solution.

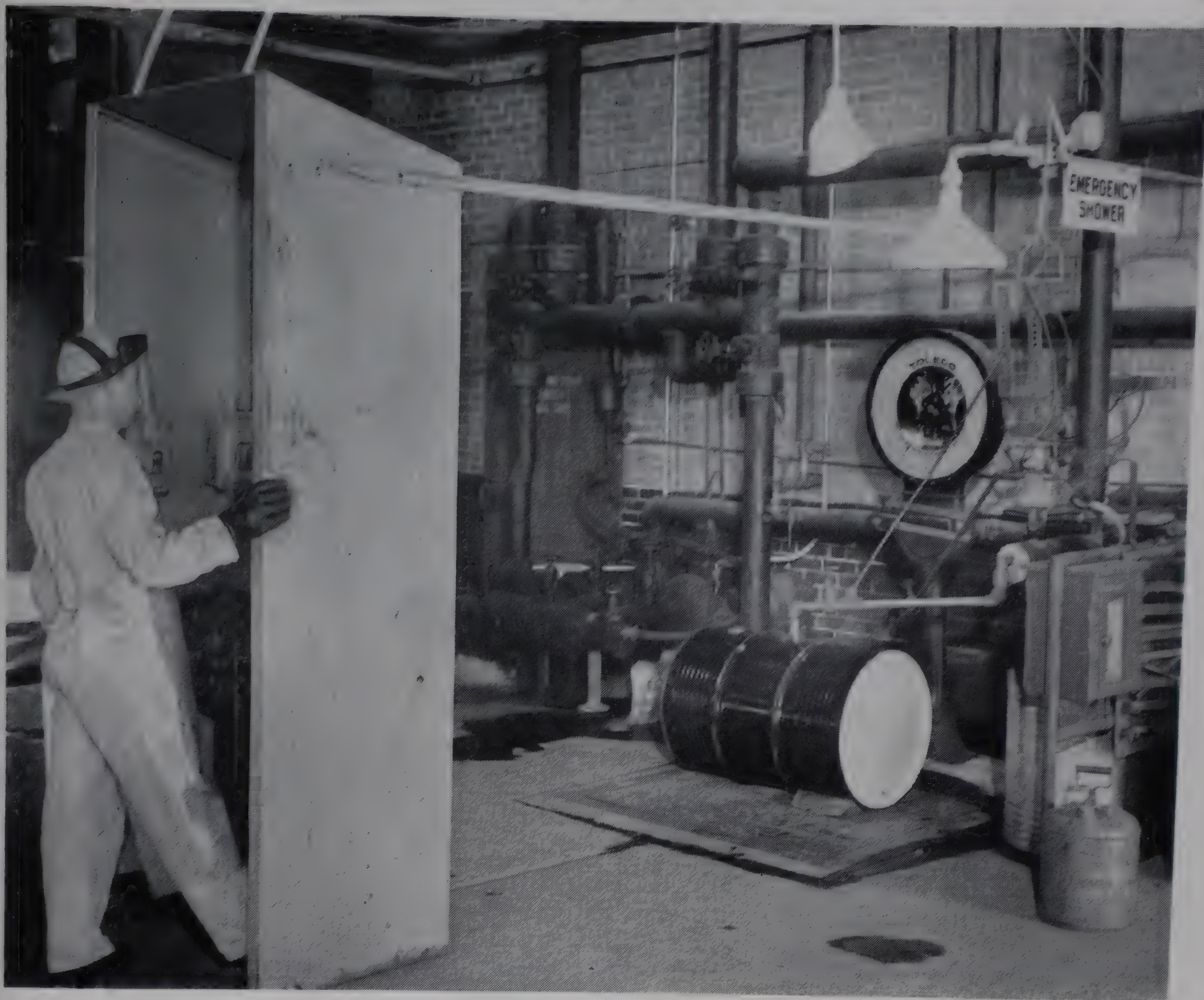
Phenol Isolation and Refining. The sodium phenate solution is held in three receiving tanks. As the solution contains a small amount of sodium hydroxide, a portion of it is fed to a cast-iron absorption tower packed with steel rings where it takes up the small amount of phenol stripped from the sulfite slurry which is a by-product of final acidification. The solution returns to the receiving tanks. Thence it passes to either of two agitated steel tanks, where there is added the weakest water fraction from the phenol refining stills; then it is pumped to the acidification tanks. The solution is cooled by means of heat exchangers. From the acidification tanks the solution is circulated through acidification towers, one of which is connected to each feed tank.

The acidification towers are vertical steel cylinders lined with lead and acidproof brick. Sulfur dioxide from the neutralizers is admitted through the side of the tower at a point about halfway up from the bottom. The solution circulated from the acidification tanks enters the top of the tower through a nozzle which gives a fan-shaped distribution to the spray. The solution absorbs sulfur dioxide and flows out the bottom of the tower to the acidification tank. Unabsorbed sulfur dioxide is discharged near the top of the tower and passes to the obnoxious vapor condenser for disposal.

The solution from the tower neutralizes the phenate solution flowing into the tank causing it to separate into two phases—



Cone-Bottom Tanks for Separating Crude Phenol from Sulfite Mother Liquor



Phenol Drum Loading System

Operator stands behind shield where filling mechanism is operated by foot pedal; removal of pressure immediately stops filling

crude phenol and sodium sulfite slurry. The mixture is pumped to vertical cone-bottomed tanks which act as gravity separators.

Sulfite slurry is drawn off the bottom of the separators and is pumped to the top of a cast-iron tower packed with pebbles. Steam is fed into the bottom of the tower at 5 to 10 pounds per square inch. Rates are balanced so that the slurry flowing from the bottom of the tower is free from any odor of phenol. The steam carries phenol out to the absorber where it is absorbed by sodium phenate.

Most of the stripped sulfite slurry is sent to evaporators for concentration to be followed by centrifugation. The solid sulfite is dried in rotary kilns and packaged in barrels or bags.

The phenol refining system consists of three sets of columns. The first of these carbon steel bubble-plate units is a dehydration column which increases the phenol concentration of the stream to above 95%. The condensate, which contains 10 to 15% of phenol, goes back to the acidification tank. The second similar type column removes the balance of the water; its condensate, which contains 70 to 75% phenol, is passed back to the dehydrating column. The phenol flows from the bottom of the second column to the U.S.P. column, from which the condensate is U.S.P. phenol. Bottoms go to a residue still where a small amount of phenol is recovered and returned to the feed tank. Some *o*-phenylphenol is reclaimed from the

bottoms. The residue is stirred with 25% caustic and is discarded.

BY-PRODUCT PROCESSING

Sulfur Dioxide. Sulfur dioxide from the neutralizer which is in excess of the requirements for acidification of the phenate is purified and liquefied for sale (Figure 2). The sulfur dioxide gas from the neutralizer passes through the Karbate tubes of a shell-and-tube cooler and thence to a series of three cast-iron drying towers packed with flint pebbles, where a countercurrent flow of sulfuric acid removes all water. The first two towers, which handle the weaker acid, are lined with lead; the third is not lined. Sulfuric acid (66° Bé.) is fed into the third tower, and acid is discarded from the first when the sulfuric acid concentration has dropped to 45%. After filtering through a bed of powdered coke the dry sulfur dioxide goes to a reciprocating compressor and is compressed to 70 pounds per square inch. The hot compressed gas is then passed through the still pot to a steel column packed with 0.5-inch carbon Raschig rings. Additional heat is applied to the still pot to vaporize refluxed liquid. The vapor, still under pressure, is condensed by means of a steel shell-and-tube condenser and the liquid goes to a split-flow box from which one stream returns to the packed column and the remaining cooled liquid is run into tank cars or cylinders for shipment.

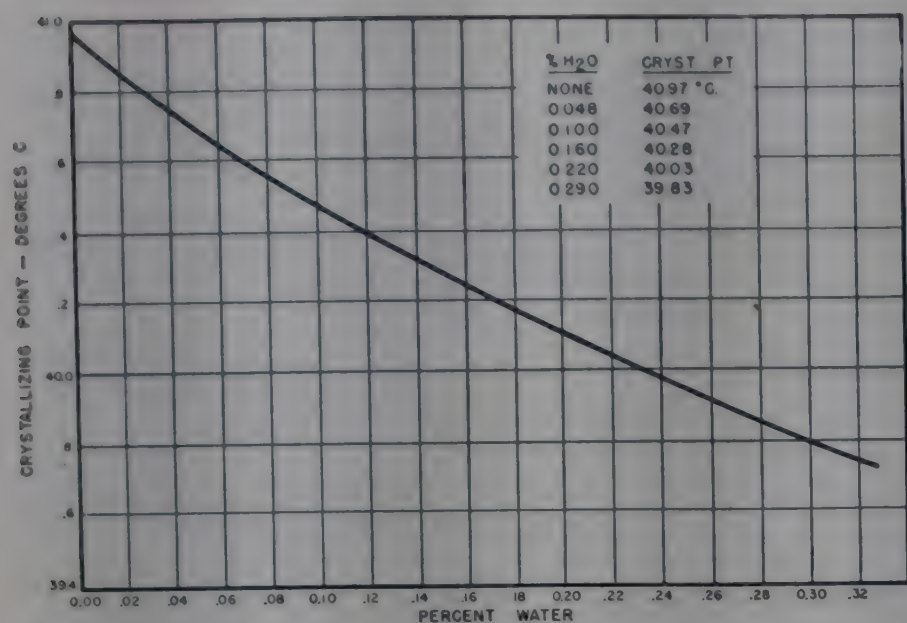


Figure 4. Effect of Moisture on Crystallizing Point of Phenol

Sodium Sulfite. Sulfite liquor (Figure 3) from the stripping column is collected in an adjustment tank where caustic soda solution is added to make the liquor distinctly alkaline. It is then passed to a cone-bottomed evaporator to which heat is furnished by two external steam heated shell-and-tube heat exchangers. The slurry from the bottom of the evaporator is run to a cone-bottomed separator from which the supernatant liquor is returned to the evaporator, and the thick slurry is fed to a basket centrifuge. The centrifugate is returned to the adjusting tank and the wet solid sulfite is carried by screw conveyor to a rotary dryer and thence to a rotary cooler. Air drawn through the dryer is passed through a dust collector before being blown into the atmosphere. The dust is returned to the wet centrifuge cake conveyor entering the dryer. After cooling, the sulfite is passed over a vibrating screen and all material passing through a 10-mesh sieve falls to the finished product bin from which barrels and bags are filled. All material retained on 10 mesh is run through a hammer mill and returned to the screen.

MATERIALS OF CONSTRUCTION

In general, equipment throughout the plant is steel or cast iron. At points where wet sulfur dioxide is handled, Tobin bronze, lead, or Haveg is used. Sodium benzenesulfonate solutions, containing small amounts of sulfur dioxide, are handled in Everdur. Nickel is used in pumps and pipes for caustic solution. Stainless steel 304 is used for the hot slurries of sodium sulfite, which has both an abrasive and corrosive action. The centrifugal separators are of stainless steel for this reason. Cast iron gives satisfactory service where sulfuric acid is used, as in the sulfonators. It is well known that iron causes discoloration of phenol. For this reason, nickel is used in handling the finally distilled product, beginning with the condensers. Steel may be used for storage and shipping where a water-white product is not required.

MATERIALS HANDLING

Almost all materials are pumped as liquids or slurries. In feeding raw materials, a constant circulation system, which provides a constant head, has proved most satisfactory for benzene and sulfuric acid. The same has been applied to the sulfonation reaction product which is fed into the neutralizers. Wet and dry sulfate and sulfite are moved by screw conveyor. Dry sulfite is also handled by conveyers of the enclosed scraper-chain type, which has the advantage of being capable of elevating material as well as moving it horizontally.

Phenol is shipped in steel tank cars of 4000- to 10,000-gallon capacities for the ordinary product and in similar nickel-lined cars where a water-white product is specified. All cars contain

heating coils which are tested before each car loading. Cars are designed to unload from the top as well as through bottom outlets. Phenol is also shipped in galvanized iron, black iron, and lacquer-lined steel drums and in 23-gallon tins. Storage tanks are of steel or nickel-clad steel.

In handling phenol, care must be taken to avoid the inclusion of water. The product is specified according to crystallizing point. As Figure 4 shows, even traces of water have a marked effect on crystallizing point.

CHEMICAL CONTROL AND SPECIFICATIONS

U.S.P. phenol from the distillation column is checked hourly and must have a minimum crystallizing point of 40.6° C. Phenol for shipment is specified as material for steel containers and tank cars or material for galvanized or lacquered drums and tins.

The standards are:

Property	Regular	Water-White
Color	White to light pink	White
Melt color	APHA 150, max.	APHA 10, max.
Solution in 10% NaOH	Clear and colorless	Clear and colorless
Crystallizing point	40.6° C., min.	40.6° C., min.
Distillation range	2° C. max. (first drop) 180° C., min.)	2° C. max. (first drop) 180° C., min.)

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Trinitrobenzoic Acid and Crude Phloroglucinol
Are Separated from Mother Liquor in
This 48-Inch Centrifuge



TNT INTO PHLOROGLUCINOL

M. L. KASTENS
Associate Editor

in collaboration with

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THIS story could be told as the chemical equivalent of the "swords into plowshares" theme. Since the end of the shooting war in 1945, Edwal Laboratories in Ringwood, Ill., have been using wartime trinitrotoluene to produce a compound with important uses in photocopying and the dyeing of textiles. Actually, Edwal has been making phloroglucinol since 1934, but the story begins with the discovery of the blueprinting process in the late 1800's. No sooner had the principles of quick and simple photocopying of line drawings been reduced to commercial practice than industrial chemists began to search for a process that would give them a black-on-white reproduction. About 1924 they found the answer in the so-called diazotype printing which produced a positive image of line drawings by developing a light-sensitive diazo compound to a colored complex by the use of a hydroxy compound (20-22). Phloroglucinol, with its three highly reactive hydroxy groups, was found to give the blackest, most stable, diazo complex and promptly was put to work.

DEVELOPMENT OF PHLOROGLUCINOL PRODUCTION

European. Kalle A.-G., a part of I. G. Farbenindustrie, achieved the first commercial production of phloroglucinol to supply a sensitized paper to another I. G. subsidiary, the Ozalid

Corporation, for use in their ammonia developing printers, in which both the diazo and the hydroxy compounds are in the paper coating (1). The van der Grinten Company in Holland developed the "moist process" shortly thereafter and also went into the production of phloroglucinol. In their process the light-sensitive diazo-treated paper is developed by a thin aqueous film of phloroglucinol after exposure (10, 16, 17).

Ammonia-developed prints were introduced into this country by the Eugene Dietzgen Company under an agreement with Kalle shortly after their development in Germany. In 1933 the marketing of "Ozalid" papers was taken over by the Ozalid Corporation, financed by Kalle. In 1929 the Charles Bruning Company, in cooperation with van der Grinten, introduced moist process printers into the United States. In the ensuing years, other companies developed and marketed other sensitized papers and direct printing machines. Most of these processes used phloroglucinol, at least in part, as their developing agent. For several years all this developer was made from phloroglucinol produced in Germany or Holland. Although "Ozalid" papers are now manufactured in this country, the coating materials are still imported from Kalle in Germany. Eastman Kodak Company made small quantities of the material, largely for their own use, in the late twenties. Their production

was hardly on a commercial scale and was suspended in 1931 when Pennsylvania Coal Products Company, established producers of resorcinol, determined to attempt commercial production of the compound by the fusion of resorcinol with sodium hydroxide (3, 5). They achieved small scale production, but their product was plagued by persistent contaminants, and production was suspended in 1935. They produced 300 pounds of phloroglucinol in that year, their highest production rate. When the plant burned down after a disastrous solvent explosion in 1937 it was not rebuilt.

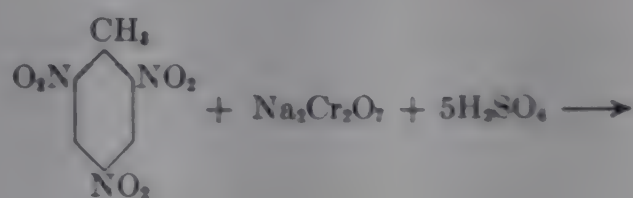
United States. With war clouds already apparent and increasing difficulty in international trade, American manufacturers of white printers became concerned over their dependence on foreign sources for developer, and in 1934 representatives of the Frederick Post Company approached Edwal Laboratories with the suggestion that they attempt to produce phloroglucinol domestically. Within the year Edwal adapted the known laboratory preparation of the compound (14, 15) to production scale and was in the phloroglucinol business. Initial production was sold at \$22 a pound to meet the price of the imported product. However, with increasing skill and volume, the company was able to reduce the price to \$12 a pound by the time the United States entered the war. The warborn scarcity of β -oxynaphthoic acid (Bona) led textile converters to consider the possibility of using the trihydroxy benzene compound as a developer for diazo black dyes. The substitution proved technically satisfactory, although somewhat more expensive, and phloroglucinol entered a new market. The volume expansion made possible by this new outlet, along with further technological advances, permitted price reductions to the present low of \$5.50 a pound for dye grade material. Even this dramatic reduction did not enable phloroglucinol to hold all its dyeing market when Bona again became available. However, it appears to be firmly ensconced in some dye works.

Technical History. Early laboratory preparations of phloroglucinol involved the fusion of di- or trisubstituted benzene compounds with alkali (2-4). It was also obtained by the hydrolysis of various natural compounds extracted from plants (19). The natural product was expensive, and the fusion product was generally of low purity. In 1897 a synthesis from trinitrobenzoic acid by reduction with tin and hydrochloric acid and hydrolysis of the resultant amine to phloroglucinol was perfected (13, 23). The preparation of phloroglucinol by the hydrolysis of the amine had been known since 1867 (18). It was the successful reduction of nitrobenzoic acid to the triamine which made the process commercially attractive. The preparation was patented in 1899 (6) by Casella and Company but apparently was not exploited at that time. About the time of the discovery of the diazotype reproduction process by Agfa, Casella was absorbed into the I. G. Farbenindustrie cartel and serious commercial production was undertaken for the first time. Initial production in Germany, and later in Holland, used the trinitrobenzoic acid-triaminobenzene route with tin and hydrochloric acid. It is still the method used in laboratory preparations in this country and for most commercial production in Europe (9), and was used by Edwal when they entered the field in 1934. Various attempts have been made to replace tin for the reduction reaction. It has been recently reported that Kalle A.-G. has developed a small unit employing the Béchamp reaction for the reduction of trinitrobenzoic acid. The acid in a low pH solution is circulated over iron, an aliquot is removed, and the remainder recycled, thus affording the first continuous technique for this reaction (12, 24). An experimental process using iron and hydrochloric or sulfuric acid has apparently also been developed at Griesheim, Germany (11).

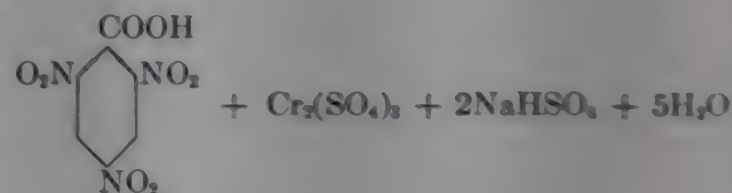
Edwal Process. Until the war the tin process was used almost exclusively both here and abroad. Before the entry of the United States into World War II, Edwal, in anticipation of wartime restrictions on the use of tin, began to investigate other

processes. By the time the wartime pinch was felt they had perfected a modification using iron in a highly acidic solution.

The process now used follows the reactions:

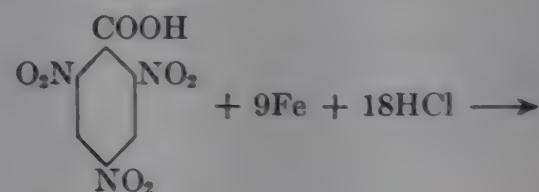


Trinitrotoluene

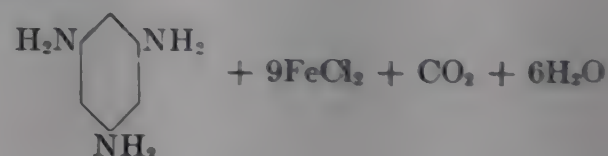


Trinitrobenzoic acid

(1)

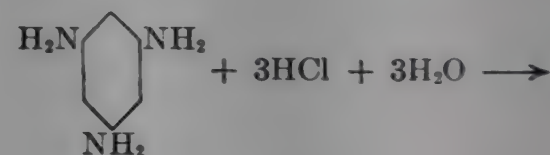


Trinitrobenzoic acid

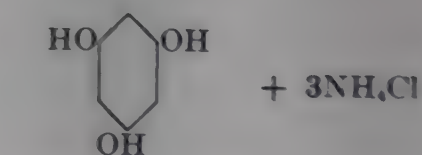


Triaminobenzene

(2)



Triaminobenzene



Phloroglucinol

(3)

The only difference between the chemistry of this process and that of the older European technique lies in the use of iron instead of tin in Equation 2. Edwal succeeded in this substitution, where others had failed, by determining the extremely close limits of temperature and acidity within which the reaction would go. In addition to eliminating the necessity for expensive tin, the modification proved to have other advantages, and is still in use although tin is once more available. In the old tin reduction it was necessary to remove most of the dissolved tin from the reaction solution before the hydrolysis step could be accomplished. The ferrous chloride produced in the new process does not inhibit the hydrolysis. Furthermore, it stabilizes the triaminobenzene formed in the reduction and reduces the number of partial-reduction products, partial-hydrolysis products, polymers, and decomposition products formed as by-products during the reduction. As a final attraction, the presence of ferrous chloride in the product of the hydrolysis tends to reduce the solubility of phloroglucinol, thus decreasing the product loss in the centrifugate.

The key to the Edwal modification is the close determination of the conditions of optimum stability for triaminobenzene. The oxidation of trinitrotoluene to trinitrobenzoic acid introduces few complications. The few per cent of yield lost at this point

can probably be explained by impurities in the TNT or by instantaneous, local, overoxidation due to inadequate agitation. The extraneous products are almost all completely volatile or soluble in the mother liquor. In the reduction step, however, slight variations in conditions—as little as a few degrees in local temperature or less than a unit of pH—can cause the reaction to digress seriously from the desired equilibrium. Under slight



Doorway of TNT Storage Magazine

TNT is stored in its 50-pound shipping cartons

variations in conditions, the trinitrobenzoic acid or any ferric chloride in the reduction kettle may act on the triaminobenzene as an oxidizing agent. Oxidation of the amine does not regenerate the nitro compound, rather the amine breaks down completely into volatile fragments. Lowered acidity in the reducer encourages partial hydrolysis of the amine and leads to internal coupling between the hydroxyl and amine groups or may result in the formation of phenolic complexes with the ferrous chloride. Overheating promotes condensation of the triamine to produce a black or brown crystalline material which is insoluble under most conditions.

Essentially the same side reactions may occur in the hydrolysis step. Excess time and/or temperature may produce polymers of phloroglucinol. Phloroglucid, the dimer, has been successfully isolated from the side-reaction products, and others in the series of higher polyphloroglucids are thought to be among the side products. If any oxidizing agent, particularly ferric chloride, is carried over into the hydrolysis kettle, polymerization is stimulated, or a complete breakdown of the product may occur. Excess acidity at this point stimulates the production of the crystalline condensation product mentioned in connection with the reduction step. Concentrations during the hydrolysis are very critical; changes of as little as 1% in any of the constituents are sufficient to unbalance the entire reaction.

EDWAL PRODUCTION

Edwal's original production was adjacent to their laboratories in Chicago. However in 1941 they purchased the present plant in Ringwood, some 60 miles northwest of Chicago, and moved their manufacturing operations there. The first of this year they moved their laboratories and administrative offices to Ringwood to consolidate operations.

The nucleus of the installation is a former milk bottling plant. Although it is now unrecognizable under a maze of additions and new buildings, it originally provided ideal facilities for small chemical production. It had large boilers, well drained concrete floors, ice-making equipment which has been put to good use, and ample water and industrial plumbing.

Raw Materials. The basic raw material for the process, although not the one consumed in the greatest quantities, is trinitrotoluene. Since the war Edwal has used military surplus TNT which is in the form of 0.25-inch flakes. However, available stores of this material are nearly exhausted, and the plant will shortly revert to the peacetime product which is a fine crystalline material obtained from Du Pont. The flakes and the crystalline material are of identical quality, meeting the following explosives grade specifications (18): TNT, 98%; melting point, 81° C.; H₂O, 0.10%; insolubles, 0.10%; acid (as H₂SO₄), 0.01%.

The TNT is received in freight car lots (about 30,000 pounds) in 50-pound boxes. The surplus material wrapped in oiled paper is packed in pasteboard boxes and shipped dry because in the flake form it will not hold water. The crystalline product, however, is wrapped in waxed paper, packed in wooden boxes, and wetted with 10% by weight of water. Shipments are unloaded by hand into a truck for transfer into the storage magazine. Maximum stock kept in the magazine is 40,000 pounds. The magazine is 14 × 14 feet and 7 feet high to the joist under the peaked roof. It has double walls, 6 inches apart; the inner wall is constructed of wooden sheathing and the outer of sheet metal. The space between the walls is filled with sand and there is a 6-inch deep tray of sand under the roof. A 9-foot high, earth bunker surrounds the magazine with an overlap at the truck entrance. The bunker is 2 feet thick at the top and slopes at 45° on both sides.

The process kettles are fed from a feed magazine holding up to 650 pounds and replenished as necessary. The feed magazine is 4 × 10 feet and 8 feet high, constructed of 0.5-inch steel plate with a flat roof. A wooden roof set on legs 6 inches above the steel roof affords protection from the direct rays of the sun. It is surrounded by a barricade identical to that around the main magazine, but of smaller diameter. Both magazines are located to meet Bureau of Mines recommendations on distances from roads and dwellings for the maximum quantities of TNT stored.

Sodium dichromate, used as the oxidizing agent, is obtained from several sources in 10,000-pound truck loads of 100-pound paper bags. The material is technical grade but must be dry to avoid lumps and be low in chloride content. A reserve of about 8000 pounds is usually kept on hand.

Sulfuric acid (99%) is delivered by Du Pont in 3350-gallon steel tank trucks from their contact plant in East Chicago. It is pumped directly from the trucks into a 8500-gallon storage tank. Feed to the process is taken directly from this tank.

The hydrochloric acid used is 21° Bé. technical grade, commonly called muriatic acid. It is also obtained from Du Pont and delivered in 6000-gallon, rubber-lined tank cars. It is stored in a 10,000-gallon storage tank which feeds a 100-gallon feed tank from which the process acid is drawn.

The iron used in the reduction is obtained as technical grade 7-mesh granules from Connelly, Incorporated. It is also delivered by trucks in lots of 20,000 pounds in 100-pound bags. Reserve storage averages 40,000 pounds. Although no special preparation of this material is required, it is essential that it have a reasonably consistent size distribution and be free of iron

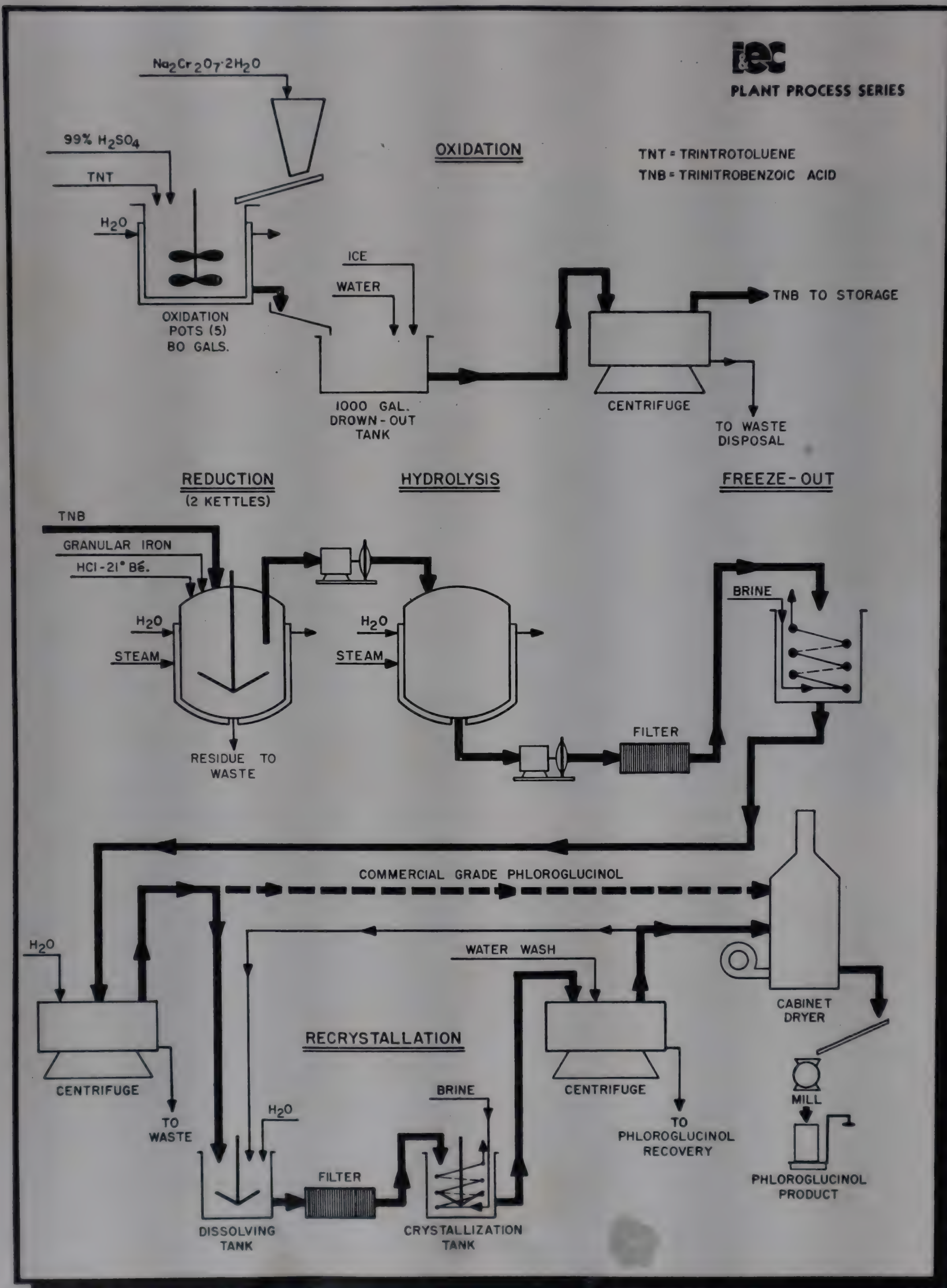


Figure 1. Process Flow Sheet for Production of Phloroglucinol at Ringwood, Ill., Plant of Edwal Laboratories



Drown-Out Tubs

Discharge from oxidation pots has a heavy sirup consistency, left, when dropped into the ice



oxide. As iron oxide is not reactive in the process, under- or over-size material has an undesirable effect on the rate of the reaction.

All but two of the materials used in this process are delivered to the plant by motor truck, although adequate railroad siding facilities are available. This method of supply is a fairly recent innovation at the plant. The switch was made largely in the interests of speed of shipment. The Ringwood plant is located within 75 miles of all the industrial districts of the Chicago area. Under this circumstance the plant management has found that motor truck deliveries can often be made within 24 hours of ordering, and sometimes within the same day. Railroad deliveries, on the other hand, sometimes require as much as 2 weeks to travel even from nearby plants. Speed of delivery has a special virtue in the shipment of sulfuric acid. The 99% acid solidifies at 10° C. During the short time required for tank car deliveries the acid will remain liquid and can be pumped from the truck to storage without heating. Acid arriving during the winter months in tank cars, however, invariably arrives in a solid state and must be held in a warming shed until it has melted. By receiving acid by truck, Edwal has been spared the expense of constructing such a warming shed over their railroad siding.

Utilities. Water for the plant is supplied from two 200-foot wells. The flow of these wells presently seems sufficient for all foreseeable future requirements. Although deionizing equipment is available within the plant, it is not necessary to treat the water for the phloroglucinol process, since the contaminants present (Table I) do not interfere with the process reactions.

Heat and steam are supplied to the plant by two stoker-fed, 125-hp. fire-tube boilers. Both heating and process steam are at 90 pounds per square inch (Table II).

Electricity is obtained from the local power company at both 110 and 220 volts. However, a 50-kilowatt, steam-driven generator is available in the plant as a standby. The 110-volt circuits are used only for lighting. All pumps and agitators in the plant

are driven by 220-volt motors to utilize the higher power factor at this higher voltage.

The phloroglucinol process requires a shift of three men and normally runs two shifts a day.

PHLOROGLUCINOL PROCESS DESCRIPTION

The first step in the production process, oxidation of the trinitrotoluene to trinitrobenzoic acid by sodium dichromate (Figure 1) is conducted in five 100-gallon welded steel pots operated in parallel. The pots are cooled during the oxidation by a water jacket circulating tap water at a temperature of about 12° C. Additional cooling is provided by two, 3-foot elliptical cold fingers suspended in each pot. The fingers are made of welded sheet steel, having axes of 5 and 12 inches and extend to within 2 inches of the bottom of the pot. They are separated by a single spreader and suspended by connecting unions at their top. Cooling water flows through the fingers and then into the jacket. The temperature of the reaction pots is automatically held between 50° and 60° C. by a control valve on the cooling water inlet operated by a diaphragm-type thermometer (12A) suspended in the reaction mixture in a thin-walled lead-sheathed copper well.

The pots are equipped with exhaust hoods primarily to remove chromyl chloride, produced from sodium chloride impurities in the dichromate. A single exhaust fan with a capacity of 1600 cubic feet per minute draws from all five hoods.

Five hundred pounds of sulfuric acid are pumped into each pot through permanently installed lines. All lines carrying concentrated sulfuric acid are within the plant buildings to avoid freezing. Fifty pounds of TNT are added to the acid by hand from the boxes in which it is received. The charge is agitated by a vertical stirrer, having two 3-bladed, 8-inch propellers, 10 inches apart.

After the TNT has been added, 75 pounds of sodium dichromate are introduced by a vibrator feeder (15A) at a rate of about

0.75 pound per minute. The feed rate can be changed manually if the temperature of the oxidation consistently tends to vary outside the established limits. During damp weather it is sometimes necessary to add bleaching and clay to the dichromate to prevent lumping and ensure free flow. During the dichromate addition, the mixture thickens, and it is necessary to increase the speed of the stirrer by means of a variable-speed drive (13A) from the initial 560 r.p.m. to a maximum of 875 r.p.m. to maintain a uniform agitation effect. The maximum stirring speed is attained about 75 minutes after beginning the addition of dichromate. At the end of the reaction, the slurry becomes too thick for uniform distribution of the dichromate by the mechanical stirrer and additional agitation must be provided by a hand operated "joggler" consisting of a metal loop which encircles the cold fingers connected to an upright rod which can be worked up and down in the kettle.

Oxidation is considered to be complete when the temperature begins to drop, usually about 4 hours after dichromate addition is begun. Agitation is continued for 10 minutes and then the charges from all five kettles are dropped simultaneously into a lead-lined, drown-out tub containing 2400 pounds of crushed ice. This chills the mixture to about 30° C., stopping the reaction, reducing the corrosivity of the acid slurry, and completing the precipitation of the trinitrobenzoic acid. After the drown out, the pots are washed, and this wash water with additional water to make a total volume of 900 gallons is added to the batch to promote ease of filtration. The slurry is then pumped to a 48-inch, center slung, centrifuge (2A) which reduces the moisture content of the precipitate to 25 to 35% by weight. The yield from this step in the process is about 82% of theoretical. Only a small amount of the trinitrobenzoic acid (3%) is lost in the centrifugate because of the low solubility (approximately 0.15 ounce per gallon) of the product at the temperature of the centrifugation. In addition to the small quantities of trinitrobenzoic acid, unreacted TNT (0.026 ounce per gallon) and side-reaction products, the centrifugate comprises 2.8 pounds per gallon of sulfuric acid, 0.2 pound per gallon of sodium sulfate, and 0.5 pound per gallon of chromium sulfate. The trinitrobenzoic acid, containing 2 to 4% impurities, largely unreacted TNT, is scooped out of the centrifuge by hand and transferred to 55-gallon, rubber-lined drums

TABLE I. PARTIAL ANALYSIS OF RINGWOOD WATER

	P.P.M.
Total solids	262
Total hardness	205
CO ₂ hardness	205
Si	20
Ca	50
Mg	19
HCO ₃	305
Other metals	Trace

TABLE II. UTILITY REQUIREMENTS (PER BATCH)

	Water, Gal.	Steam, Lb.	Power, Kw.-Hr.
Oxidation of trinitrotoluene ^a	61,500	..	127
Reduction of trinitrobenzoic acid	7,000	1000	76
Hydrolysis of triaminobenzene	2,500	1600	92
Crystallization	2,500	..	18
Single recrystallization	4,000	1200	46
Drying	27
Total	77,500	3800	386

^a Adjusted to equate with reduction batch.

which have been secured to 4-wheeled dollies for ease of movement.

The product batches from the oxidation average 225 pounds, dry. The charge to the next step, the reduction, is 864 pounds so it is necessary to run the two steps on different time schedules. When starting up the plant the oxidizers are started 2 days before the rest of the process and these 2 days' production of trinitrobenzoic acid are sealed in the rubber-lined, wheeled drums and stored in the warehouse to provide a cushion to absorb rate discrepancies between the two steps of the process and to eliminate the necessity of shutting down the entire process if the oxidizers are out of operation. After both sections are in operation trinitrobenzoic production waiting to be used in a reducer charge is stored in the rubber-lined drum right on the processing floor.

Since there is some danger that stored trinitrobenzoic acid may partially dry out as the water settles to the bottom of the drums, this material is not allowed to stay in storage more than 2 weeks.



Two Glass-Lined Reduction Kettles, Run in Parallel

Hydrolysis vessel is identical, but of larger size

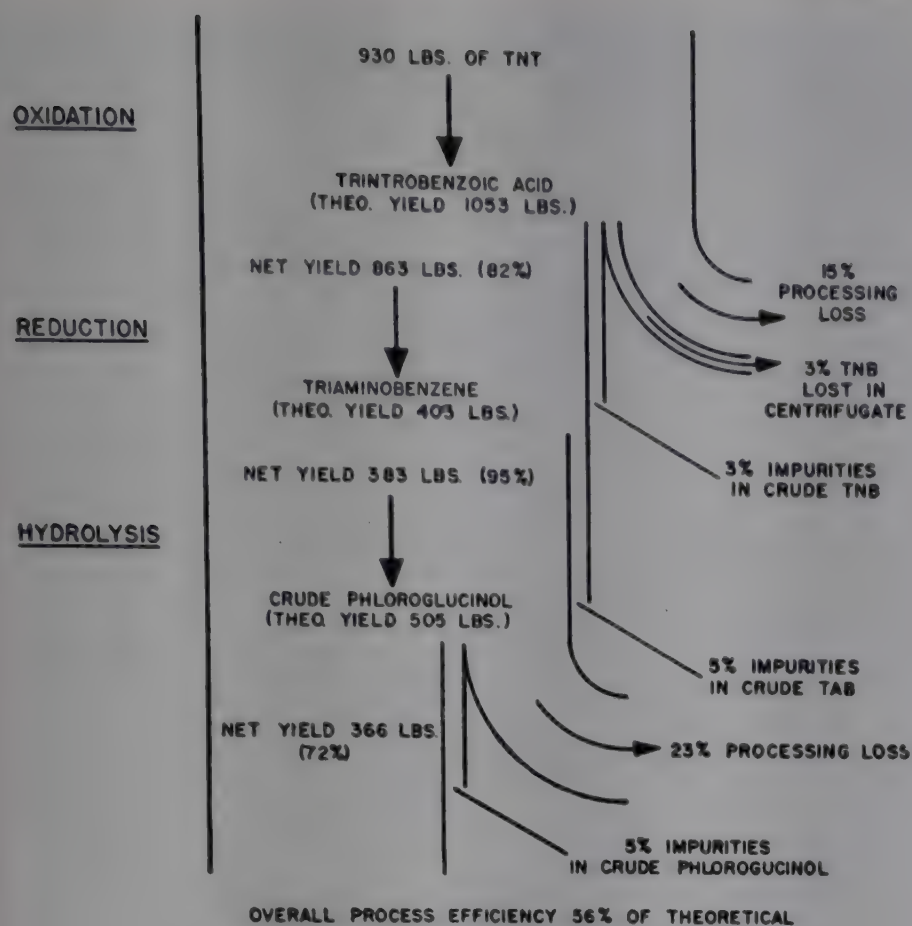


Figure 2. Materials Balance

After this period the oldest acid from the stored cushion is fed to the reduction step and replaced by current oxidation product, and the reserve is maintained on a rotating basis. The reduction step is carried out in two 750-gallon glass-lined kettles, which, like the oxidation pots, are always run in parallel. The reducing kettles are jacketed with inlets into the jackets for both steam and cooling water. Although steam is supplied at 90 pounds per square inch pressure, relief valves on the jackets are set for 75 pounds per square inch. Steam is used merely to heat the water bath rather than provide a true steam jacket. The temperature during the reaction is held at about 90° C., cooling or heating when necessary. Usually the heat of reaction is sufficient to maintain the optimum temperature without using additional heat. However, some heating is sometimes necessary to initiate the reaction.

An absorption tower using a water spray over 4 feet of 1-inch Raschig rings is connected to the exhaust from the kettles to remove any hydrochloric acid fumes which are driven off. The tower is 6 feet high by 36 inches in diameter and of wooden construction. The water spray is fed at a rate of 8 gallons per minute. Discharge water (pH <1) is piped directly to the clear water lagoons of the waste disposal unit to dilute the final waste discharge.

To begin the reduction, 500 gallons of 21° Bé. muriatic acid are run into the reduction kettles and the 864 pounds of trinitrobenzoic acid are scooped in from previously weighed transfer drums. Fourteen hundred pounds of commercial iron powder, which will act as the reducing agent, are introduced in small portions throughout the entire period of reduction. Decarboxylation occurs simultaneously with the reduction so that the product from the reducing kettles is triaminobenzene. The yield is usually about 95% of theoretical. The primary side-reaction products are polymers of triaminobenzene which represent about 5% of the total crude yield, and sometimes run higher.

The reduced mixture is decanted from the iron sludge and pumped to a 2000-gallon glass-lined vessel. One hundred gallons of water are added to ensure solution of the aminobenzene and ferrous chloride, and additional muriatic acid is added to lower the pH. A water jet is sometimes used to knock down foam in the reduction kettles. When this is necessary, the water so used is metered and subtracted from the amount added at the completion of the reduction. Heating to 108° C. in this kettle and holding at that temperature for 20 hours hydrolyzes the amine groups

to hydroxyl and produces the crude phloroglucinol in solution. The hydrolyzed solution is filtered hot through a 24-inch, wooden, through-washing, 15-plate filter press to remove residual iron sludge and small amounts of free carbon and tars produced in the reduction and hydrolysis. The filtrate is pumped into two 800-gallon wooden tanks equipped with internal brine coils. The solution is chilled in a period of 6 hours to 10° C. to precipitate the crude phloroglucinol. The cold slurry is dropped into the same 48-inch centrifuge used to filter the trinitrobenzoic acid from the oxidation step. Centrifugation reduces the water content to 10 to 15%. The effluent contains less than 0.1% of phloroglucinol, iron chlorides, and hydrochloric acid. The batch yield is usually about 400 pounds; 95% of this is phloroglucinol dihydrate which represents 70 to 75% of the theoretical yield (Figure 2).

Phloroglucinol, which is intended for consumption by the textile dyeing industry, graded commercial, is washed in the centrifuge with 25 gallons of water, transferred by hand to 30-gallon stainless steel batch cans and sent directly to the dryers. That destined for use in diazotype developers or for analytical reagents, in which high purity is required, is redissolved in water and recrystallized.

TABLE III. SPECIFICATIONS OF PHLOROGLUCINOL PRODUCTS

	Commercial	Technical	Chemically Pure
Appearance	Tan to brown crystals	White to cream crystals	White crystals
Clarity of 1% soln. in H ₂ O	No appreciable turbidity	No appreciable turbidity
Melting point, ° C.	200-216 ^a	>212° C.	>214° C.
Melting range, ° C.	3	<3° C.	<2° C.
Ash, %	<3.0%	<0.2%	<0.1%
Fe ⁺⁺	None ^b	None ^b
Fe ⁺⁺⁺	None ^c	None ^c
H ₂ O, % ^d	25 ^e	<23
Taste	Sweet	Sweet
Odor	None	None
Alcohol solubility, %	0.02

^a U. S. Pharmacopoeia method.

^b Turnbull's blue.

^c Prussian Blue.

^d Includes 22.2% H₂O of crystallization.

^e Weight loss at 110° C.

The washed crude material which will be recrystallized is transferred from the centrifuge to batch cans and dumped into a 300-gallon glass-lined dissolving tank where 110 gallons of de-ionized water at 100° C. are added, and the solution is agitated for 30 minutes. The solution is allowed to cool to 90° C. and filtered through duck-cloth filters in a 12-inch filter press. From the filter the solution goes to the 300-gallon glass-lined crystallizing tank where it is chilled to 20° C. by internal brine coils. The resulting slurry is then pumped back to a centrifuge where the material is spun to 10% water by weight. The product is scooped from the basket into batch cans and if it is of satisfactory purity it is sent to the dryers. If a product of higher purity is desired the recrystallization procedure is repeated. One or two recrystallizations are made on the technical grade intended for photocopying use. The chemically pure reagent grade product sometimes requires as many as four recrystallizations to meet specifications. Centrifugate from the first recrystallization is returned to the hydrolysis kettle to reclaim as much as possible of the dissolved phloroglucinol and the soluble extraneous products. Centrifugate from the second run is concentrated and refiltered to yield a crude product which meets the specifications for commercial phloroglucinol. When additional recrystallizations are required the centrifugate is recycled to provide a solvent for dissolving crude product for the first recrystallization.

Both the commercial grade and the recrystallized phloroglucinol are dried on 24 × 28 inch glass plates carried in a special rolling



Waste Disposal Plant

Treatment tank, foreground, discharges to sludge pits; clear-water lagoons are behind trees, background

rack built to hold 25 plates. The plates are loaded by hand with a layer of about 2 inches of the wet powder (about 7 pounds per tray) and the racks are rolled into a room temperature drying chamber. Heated drying would cause the phloroglucinol to lose its two molecules of water of hydration. In 15 to 20 hours the forced air circulation in these chambers dries the product to the pure dihydrate crystals. The dryer is equipped with a 2400-cubic-foot-per-minute blower which produces an air velocity of about 80 feet per minute.

When the drying is complete the racks are removed from the dryer and the plates dumped, again by hand, into a small hammer mill to break up any soft aggregates which may have formed. The product as it comes from the mill is about 20 mesh. It is fed directly into 100-pound drums, lined with polyethylene bags, for shipment. Although many other Edwal products are packaged in small containers for direct consumer use, all phloroglucinol is shipped in large containers for further formulation.

WASTE DISPOSAL

The phloroglucinol process affords a major waste disposal problem. Filtrates from the two centrifugings are highly acidic and contain appreciable quantities of chromium and iron. The most difficult contaminant, however, is the phloroglucinol itself, which tends to react with effluents from other processes to produce highly colored complexes.

Several attempts have been made to recover valuable components in the effluents or to sell the solutions "as is." Unfortunately none of these has been successful. The undiluted filtrate from the oxidation step is 67% sulfuric acid and contains 19% of chromium sulfate. If allowed to stand undiluted, the sodium bisulfate formed in the oxidation precipitates and settles out. The solution is obviously suited to steel pickling operations and plant tests run in American Steel and Wire Company's sheet mills in Waukegan, Ill., indicated that in addition to satisfactory

pickling performance, the solution deposited a chromate coating on the sheet which gave it appreciable corrosion resistance. However, the diluted solution as it presently comes from the drown out is not acidic enough to serve as a pickling liquor. If the solution is not diluted at this point the removal of liquids from the crude trinitrobenzoic acid is very difficult because of the thick, almost gelatinous, nature of the undiluted slurry. Transportation difficulties also decrease the practicability of utilizing this filtrate. In order to get the solution to the steel mills, some 20 miles distant, it would be necessary for Edwal to secure corrosion-resistant tank trucks. This expense is not justified by the relatively small amount of the effluent which is produced.

Other experimental work with this solution has been aimed at reacting the high chromate content to produce a chrome pigment. However, up to this writing it has not been successful.

The effluent from the final centrifuging contains 430 grams of ferrous chloride per liter and 40 grams of ammonium chloride per liter. The ferrous chloride can easily be converted to ferric chloride by treatment with chlorine gas to yield a solution similar to that used in large quantities for sewage treatment. Investigations with the Sanitary District of Chicago indicated that the effluent could be used, but the project was defeated by the same considerations of transportation and inadequate supply which pertained to the oxidation filtrate. Economic use of these waste liquors is one of the advantages Edwal can hope to obtain from possible increased production in the future.

Waste from the Ringwood plant is discharged into a small stream running through the site where flow varies seasonally between 100 and 200 gallons per minute. When the plant first went into operation, waste was discharged, untreated, into this stream. However, as the operations were enlarged it became necessary to install a waste treatment unit (?). At the present operation rate, liquid waste discharge from the plant approaches 40 gallons per minute for a 24-hour day. The waste liquids from



Finished Phloroglucinol in Drying Racks

Product is scraped into small hammer mill from which it feeds directly into shipping container

all processes are collected alternately in one of two 5000-gallon vertical wooden tanks. The mixture in these tanks is agitated slowly by a motor driven paddle (11A) made of a length of 2×4 mortised into an 8-inch square wooden shaft. Oxidizing agents present in the waste and exposure to the atmosphere oxidize the effluent. When one tank is two thirds full the plant discharge is switched to the other and dolomitic lime is added to the first until the pH is raised to about 9 to precipitate the heavy metal oxides. Dolomitic lime is used rather than regular lime because it has a higher per weight activity and is hence cheaper on a performance basis. Toward the end of the neutralization, ground limestone is added to restrict caking of the precipitate and increase turbulence in the tank. After the neutralization is complete the batch is pumped to one of two sludge pits. Most of the precipitate settles out at this point. At the lower end of the sludge pit the effluent filters through a gravel bed to a sump and thence to one of the two settling lagoons where the fines are allowed to settle out. Three quarters of the way down the lagoons there is a gravel barrier with a 4-foot over-flow spillway through which the effluent passes to the clear water lagoons. Samples from these final lagoons are analyzed for heavy metals, cyanide, total solids, and pH. Analyses usually show no chromium, no ferric iron, 0 to 40 p.p.m. ferrous iron, and from 0.25 to 0.75 gram per liter of total solids. The overflow from these lagoons discharges into the creek. The regular appearance of minnows in the creek at the point of discharge certifies the biological inactivity of the effluent.

The twin sludge pits and lagoons are intended to be used alternately. However, only one settling lagoon has been used in the 2 years in which the waste plant has been used. The sludge pits must be cleaned about once a month. When one pit becomes filled with about 10 feet of sludge, the discharge is switched to the other, and the first is allowed to drain and dry out until the other pit has become almost filled. About a week before the pit in use becomes filled a drag line is brought in to scoop the sludge out of the drained pit and load it onto trucks for transportation to a dumping pit. About 500 yards of sludge, mostly calcium sulfate, and iron and chromic oxides, must be disposed of each time a pit is cleaned. A private dumping pit is now available, but when this excavation has been filled it will be necessary for Edwal to purchase some nearby wasteland to dispose of their waste sludge.

CHEMICAL CONTROL

Control testing in the phloroglucinol process is relatively simple. The crude trinitrobenzoic acid from the first centrifugation is assayed for water content by codistillation with a petroleum solvent. Unreacted trinitrotoluene is determined from an ether extract of the crude trinitrobenzoic acid. A water extract is titrated against standard base and acidity calculated as per cent sulfuric acid.

During the later stages of the reduction step samples from the kettles are taken at regular intervals and titrated for per cent of free hydrochloric acid. No other tests are made on this step. The liquor at the end of hydrolysis is checked with a sensitized diazo paper to ascertain whether phloroglucinol has been actually produced. This paper is specific for phloroglucinol giving a red color. Other compounds will produce different colorations. The pH of the liquor at this point can be determined with an electronic meter since it is only slightly acid.

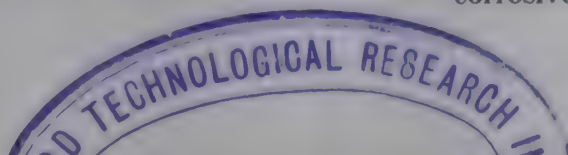
Except for strength determinations by titration on the acids used, no raw material control is exercised. Phloroglucinol products are analyzed to meet specifications given in Table III.

Considerable work is being done in the company's laboratories on spectrophotometric methods of analysis using the well known color reactions of phloroglucinol and related compounds. This work seems to be progressing satisfactorily and the results will probably be applied in the near future to give closer control of the synthesis processes and provide additional data about its exact mechanism.

MATERIALS OF CONSTRUCTION

Most of the solutions and slurries involved in the commercial preparation of phloroglucinol are highly acidic and require special precautions against corrosion. Pipe materials used vary with the service. Lines which carry concentrated sulfuric acid are constructed quite satisfactorily of ordinary steel pipe. However, after the drown-out tub in which the acid slurry is diluted, neoprene hose (5A) is used for temporary connections to the centrifuge. Muriatic acid is conveyed to the process area in neoprene-lined steel pipe, but the discharges from the reducing tank to the hydrolyzer and from the hydrolyzer to the freeze-out tubs are neoprene hose to provide flexibility in connections. The short line from the freeze outs to the centrifuge is of bronze (10% zinc, 10% tin, 80% copper). The effluent from the centrifuge is carried to the waste disposal plant in vitrified sewer tile since it must resist both the dilute sulfuric acid effluent from the oxidation-step filtration and the hydrochloric acid from the final product centrifuging. The brine coils on the freeze-out tubs are of a silicon-manganese bronze (1A). The pumps in the plant are centrifugal or diaphragm types. The material of their construction varies with the service. The centrifugal pumps which feed the concentrated sulfuric acid to the oxidizing pots are made of cast iron. The pumps between the drown-out and the centrifuge are a high chrome-high nickel stainless steel (20 chrome, 24 nickel, 3 molybdenum, 5 manganese, 1.75 copper). In the reducing and hydrolyzing cycle where hydrochloric acid solutions must be handled, diaphragm pumps with neoprene diaphragms are used (10A). Similar diaphragm pumps are used to handle the waste liquors to and in the waste disposal unit (7A). Hydrochloric acid is delivered from the storage and feed tanks by air pressure introduced into the tank head. All other flows are by gravity.

A large variety of valves are also used to provide the necessary service in the various steps in the process. The sulfuric acid lines to the oxidizing pots are controlled by iron plug valves (14A). The flow from the oxidizing pots passes through ceramic cocks (4A). Hydrochloric acid to the reducing kettle is fed by neoprene diaphragm valves (6A). The lines in the reduction-hydrolyses section and those in the waste disposal system are neoprene pinch valves. These valves have proved especially satisfactory for corrosive service throughout the Edwal plant and have been used



increasingly. They have been especially effective in handling slurries which tend to cake in the valve. In the past operators rodding through such jams very often cracked the ceramic lining of the valves or tore a rubber lining. Pinch valves which can be freed from the outside of the line are not subject to this hazard.

As they handle only concentrated acid, the oxidation pots can be made of ordinary sheet steel. The centrifuge basket is of Type 316 stainless steel. The down-out tub is lead-lined with 8-pound ($\frac{3}{16}$ -inch) lead. This lining lasts about 2 years before complete replacement is necessary. All other process vessels are glass-lined, except the freeze-out tubs which are made of wood. Muriatic acid is stored in and fed from rubber-lined tanks. Sulfuric acid, because of its high concentration (99%) is satisfactorily held in ordinary carbon steel tanks.

Filter bags for the centrifuge are woven of vinyon. Wool bags were originally used, but the synthetic fiber was found to last two to three times longer and cost only about 75% more. The plate-and-frame filter uses vinyon N filter cloths. Both wool and regular vinyon have been tried for this service in the past. The vinyon N has proved to have six to seven times the life expectancy of wool. Vinyon proved unsatisfactory because of its loss of tensile strength in the hot solution.

SAFETY PROCEDURE

Despite its apparent hazards, the phloroglucinol process has a good safety record. This is partially due to the fact that the hazard is more apparent than real. Under the conditions of the process TNT is not likely to explode, and an explosion of any of the intermediate compounds is even less likely. Several small TNT fires have occurred in the plant but without serious consequences and with little danger of explosion. In fact, on one occasion, when an autoclave near the oxidizing pots exploded and started a fire, the TNT oxidizing pots were among the few things that did not blow up in the ensuing destruction of the area. Otherwise the clean safety record can be credited to a careful but simple safety procedure.

All tools used in the handling of TNT are sparkproof. Care is taken to ensure that the TNT is thoroughly dissolved in the acid before any dichromate is added to the oxidizing pots. Since addition of dichromate is necessary to maintain the oxidizing reaction, numerous provisions are made for cutting off this feed if any operating conditions go astray. A maximum temperature switch (8A), which will cut out the feeder if the temperature exceeds a certain limit, is installed in the pot. A pressure-operated switch (9A) in the cooling-water line performs the same function if the cooling-water stream is interrupted. The agitator is likewise equipped with a safety switch which cuts out the dichromate feeder if the power supply to the agitator motor is interrupted; in the absence of proper stirring, lumps of dichromate will collect and cause local overheating which will quickly ignite the unconverted TNT. In all cases when the feeder is cut out by the automatic control, a red light lights above the pot concerned and a horn blows outside of the oxidizer room.

Since a leak of water from the water jacket into the concentrated acid of the oxidizing mixture would most certainly result in an explosion from one of a number of causes, the oxidation pots are carefully inspected every night for pits on their inner surface. Such pitting always occurs in the welding beads at the seams and can be repaired by rewelding the bead. Over weekends or on other occasions where the pots will be idle for more than a few hours, they are filled with dilute sodium carbonate solutions to prevent the formation of highly corrosive dilute sulfuric acid on their inner surfaces from the accumulation of atmospheric moisture.

No particular safety hazards are involved in the other steps of the process, therefore no other special safety devices are installed.

PRESENT USES OF PHLOROGLUCINOL

A small quantity of c. p. phloroglucinol is used as a laboratory reagent where it forms colored phenolic complexes with carbonyl groups in pentoses and other naturally occurring substances. However, the great majority of the phloroglucinol produced by the Edwal plant, which is all that is produced commercially in this country, is used in two applications. The first, and only application until recent years, is as a developer in the familiar black-and-white reproduction machines of various types. In the moist

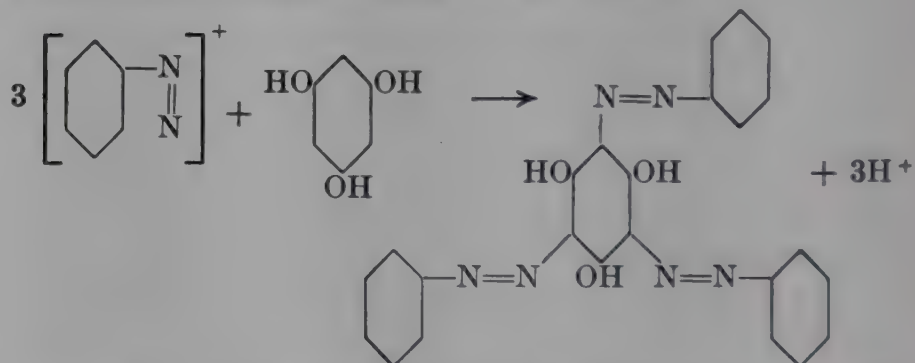


TNT Storage Magazine

Capacity, 40,000 pounds

process, the sensitive paper is coated with a diazo compound which is decomposed by light. When this paper is placed under a line drawing on a translucent sheet and exposed, all the diazo except that which has been protected by the shadow of the original is decomposed. Then when the sheet is moistened with a solution containing phloroglucinol, the remaining diazo reacts to form a large molecule which has a characteristic black color.

The reaction between phloroglucinol and aniline diazo, as follows, is shown to illustrate the reaction. In actual practice a wide variety of light-sensitive diazos are used:

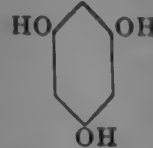
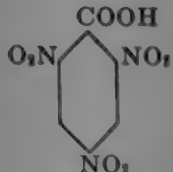
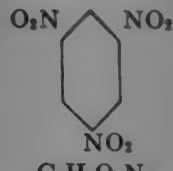
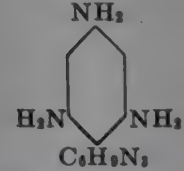
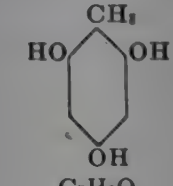
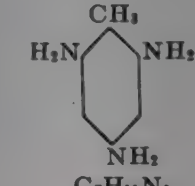
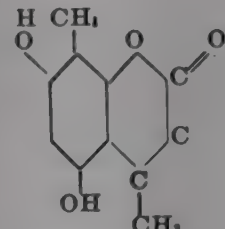
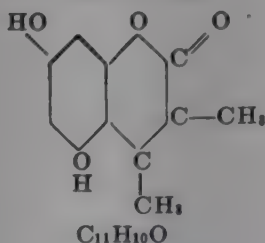
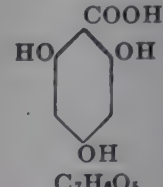
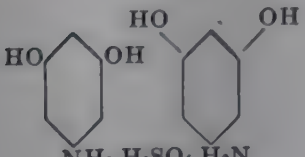


The dry process utilizes somewhat similar chemistry. In this type of printing the diazo and the hydroxy compound are both contained in the coating of the photographic paper. However, the diazo is stabilized by the presence of acid in the coating and is unreactive to the hydroxyl group. Photodecomposition is effected as in the moist process and the exposed print is subjected to ammonia vapors which neutralize the acid and activate the diazo resulting in the formation of the black complex. Phloroglucinol was once widely used in this process but in recent years it has been supplanted to some extent.

The product compound is extremely stable and provides a clear and permanent image. Resorcinol and other polyhydroxy compounds will form similar complexes, but they do not have the desirable jet black color produced by the triple chromophores of phloroglucinol. The three combining sites of the phloroglucinol also give it the added advantage of higher per weight activity than the dihydroxy compounds.

The chemistry of phloroglucinol's second use is identical with that of its use in photocopying. Certain black diazo dyes have been found to be effectively developed by phloroglucinol, particularly on acetate rayon fabrics. It gives a "cold" black comparable to the best produced by Bona with superior light and

TABLE IV. PROPERTIES OF PHLOROGLUCINOL DERIVATIVES

Phloroglucinol (1,3,5-trihydroxy benzene)	 $C_6H_3O_3 \cdot 2H_2O$	White rhombic crystals; m.p., $218^\circ C$.; b.p., sublimes (decomp.); mol. wt., 126 (dihydrate, 162)	Preparation: reduction of trinitrobenzoic acid with iron and HCl, hydrolysis in situ Exhibits high reactivity in condensation reactions; fastest diazo coupling agent known; carboxylates readily by heating in Na_2CO_3 solution
2,4,6-Trinitrobenzoic acid	 $C_7H_3O_8N_3$	Mol. wt., 257; m.p., $210^\circ C$., with decomposition	Preparation: oxidation of TNT with $Na_2Cr_2O_7$ in H_2SO_4
1,3,5-Trinitrobenzene	 $C_6H_3O_6N_3$	Mol. wt., 312; m.p., $121-122^\circ C$.	Preparation: decarboxylation of trinitrobenzoic acid in alkali solution at $85^\circ C$.
1,3,5-Triaminobenzene (available as the trihydrochloride)	 $C_6H_3N_3$ $[(C_6H_3N_3)_2 \cdot 3H_2O]$	Gray crystals; m.p., $129^\circ C$. (monohydrate, $82^\circ C$.; mol. wt., 123)	Preparation: reduction of trinitrobenzoic acid with iron and HCl Highly reactive in condensation reactions; undergoes hydrolysis in weak acids to give phenolic derivatives; base is stable to alkalis; undergoes resinification at pH 4-6
Methyl phloroglucinol (2,4,6-trihydroxytoluene)	 $C_7H_8O_3$	White crystals; m.p., $207-208^\circ C$.; mol. wt., 140	Preparation: reduction of trinitrotoluene with iron and acid at $70-80^\circ C$., hydrolysis in situ Couples readily with diazo; carboxylated readily by heating in Na_2CO_3 solution; condenses easily with active carbonyl groups; extremely reactive in other condensation reactions
2,4,6-Triaminotoluene (available as the trihydrochloride)	 $C_7H_{11}N_3$	M.p., $120^\circ C$.; mol. wt. 137.18	Preparation: iron-HCl reduction of TNT, neutralized with NaOH and extracted with chloroform Little tendency to hydrolyze in strong acid solution; undergoes resinification at pH 4-6; fairly stable in strong alkali; light-sensitive, deteriorates in storage; possible ion exchange resin component, wetting and frothing agent, coupling component in chrome colors for wool, organic intermediate, photographic developers
5,7-Dihydroxy-4-methylcoumarin	 $C_{10}H_8O_4 \cdot H_2O$	Yellow, free-flowing crystals; mol. wt. (hydrate), 210; m.p. (hydrate), $280-286^\circ C$.; H_2O , 9%	Fluorescent, absorbs ultraviolet; whitening agent in dyes, soaps, plastics; structural similarity to coumarin compounds used pharmaceutically as anti-coagulants
5,7-Dihydroxydimethylcoumarin	 $C_{11}H_{10}O$	Yellow, free-flowing crystals; mol. wt., 206; m.p., $300-305^\circ C$.; H_2O , 5%	Same as 5,7-dihydroxy-4-dimethyl coumarin
Phloroglucinol-carboxylic acid	 $C_7H_6O_5$	Mol. wt., 170, decomposes to phloroglucinol at approx. $100^\circ C$
Phloroamine sulfate	 $NH_2 \cdot H_2SO_4 \cdot H_2N$ $2(C_6H_3O_3) \cdot H_2SO_4 \cdot 2H_2O$	Light yellow powder; mol. wt., 356

perspiration fastness. Wartime shortages of Bona and the steady decrease in the price of phloroglucinol led to its introduction in this field. The shortages have ended, but the simplified operating procedure possible with phloroglucinol plus its wide permissible pH range have enabled it to retain a substantial part of its market in the dyeing industry.

FUTURE PROSPECTS

Further price reductions may enable phloroglucinol to reclaim more of its wartime dyeing market. Since phloroglucinol goes three and one half times as far as Bona as a dye developer its present price (\$5.50 per pound) is not far from competitive with Bona currently quoted at about \$1.20 per pound. With or without a price drop, preliminary investigations indicate that phloroglucinol may find additional use in the dye house. It is probable that with properly modified technology it can be used to develop acetate blues, and it also shows promise in the dyeing of Orlon, and cotton and wool fabrics. A lower price may also enable it to compete economically in some new areas. Edwal is aiming, with considerable confidence, at a price of \$2 a pound. At this price they think that its ability to form resinous complexes with aldehyde groups will bring it into use in the manufacture of special resins. They see it as the ultimate member of a commercial phenol-resorcinol-phloroglucinol series. It can function as an accelerator in the setting of resins and resin-base glues, acting as a self-consuming catalyst. Its high activity would permit exceptionally rapid setting formulations even for cold-setting applications. Its highly concentrated activity may also make it valuable in the synthesis of ion exchange resins. Phloroglucinol carboxylic acid, for instance, will form resins with high concentration of carboxyl groups.

As the only triple-substituted, symmetrical benzene compound commercially available, phloroglucinol may have unexplored potentials in organic synthesis. Its three active groups suffer almost no steric hindrance. Its low toxicity indicates possibilities in pharmaceuticals or synthetic flavoring materials. A phloroglucid, for instance, is known to be in the bitter principle in hops. Certain related compounds have proved pharmaceutical value.



Ice Field

Brine lines which cool ice field also chill freeze-out and crystallizing tanks

Satisfactory procedures for the manufacture of many derivatives of phloroglucinol (Table IV) are known and the intermediates of the process, trinitrobenzoic acid and triaminobenzene, can easily be isolated from the process now in use. Edwal's research department is continually seeking uses for these compounds. The carboxylic acid derivative of phloroglucinol, easily prepared by treating with potassium bicarbonate at temperatures above 60° C., has promise as an analgesic because of its similarity to salicylic acid. Phloroamine, in which one hydroxyl group is replaced by an amino group by treatment with ammonium hydroxide at atmospheric pressure, is of possible interest as an antitubercular.

Methyl phloroglucinol has been briefly investigated as an intermediate in the manufacture of chrome colors for wool—for example, a black chrome color for this purpose is prepared by coupling 2 moles of diazotized 4-chloro-6-sulfo-2-aminophenol to methyl phloroglucinol. In addition, limited experimental data indicate that methyl phloroglucinol may be made into dyes of a gallocyanine type possessing high tinctorial power. Its ability to form cold-setting polymers and its relatively high activity as an antioxidant in preventing the rancidification of edible oils are also of interest.

Experiments show that triaminotoluene is also a promising coupling component in making chrome colors for wool. Several brown chrome colors which show good quality have already been prepared from this compound. Like methyl phloroglucinol, triaminotoluene can also be used as a resin intermediate in several types of polymers.

Commercial interest in triaminobenzene may possibly develop along two lines: as the azo dyestuff coupling component in the manufacture of dyes, and as a pharmaceutical intermediate in the manufacture of antipyretic compounds.


Most of the promise of phloroglucinol is dependent on still lower prices. However, a technology which has cut the price to one fourth of that charged for the product of an established foreign installation may reasonably be expected to find technological short cuts to force the price down still further. And, of course, to a certain extent, increased volume of production brings its own financial reward and will inherently effect some decrease in production cost.

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PROCESSING EQUIPMENT

- (1A) American Brass Company, Waterbury, Conn.
- (2A) American Machine and Metals Co., Moline, Ill., T.33172, 48 inch center slung centrifuge.
- (3A) Fitzpatrick, W. F., Co., Chicago, Ill., Model D comminuting machine.
- (4A) General Ceramics and Steatite Corp., Keaseby, N. J., ceramic cocks.
- (5A) Goodall Rubber Co., Philadelphia, Pa., Chemite duct.
- (6A) Hills McCanna Co., Chicago, Ill., Saunder-type valves.
- (7A) Marlow Pump Co., Ridgewood, N. J., single diaphragm "Mud Hog" 303-S.
- (8A) Mercoid Co., Chicago, Ill., Type DA 38-3 temperature controller.
- (9A) *Ibid.*, pressure operated control switch.
- (10A) Oliver-United Filter Co., New York, N. Y., Oliver diaphragm pump #3 ODS, L-42687.
- (11A) Patterson Machinery and Foundry Co., East Liverpool, Ohio 3-hp. Unidrive agitator motor.
- (12A) Powers Regulator Co., Chicago, Ill., No. 11 temperature regulator valve.
- (13A) Reeves Pulley Co., Chicago, Ill., No. 28½, Reeves drive.
- (14A) Rockwell Manufacturing Co., Nordstrom Valve Div., Pittsburgh, Pa., iron plug valves.
- (15A) Syntron Co., Homer City, Pa., Syntron feeder, Model FM010
- (16A) The Mine and Smelter Supply Co., Denver, Colo., Masco-Grigsby pinch valves.
- (17A) Worthington Pump Co., Harrison, N. J., Worthite.



COMMERCIAL DEVELOPMENT OF GLYOXAL

Glyoxal Operating Equipment at Carbide and Carbon Co., South Charleston, W. Va.

Tall column is reactor; quencher is on ground floor at right and converter on upper level; drum-loading building in background

J. F. BOHMFALK, JR.

Associate Editor

in collaboration with

R. W. MCNAMEE AND R. P. BARRY

Carbide and Carbon Chemicals Co., Division of Union Carbide and Carbon Corp., South Charleston, W. Va.

PRODUCT development can mean either of two things: developing a chemical for a contemplated market or developing a market for a special chemical. These procedures are complementary and neither needs to predominate. Product development is the logical extension of the research laboratory, and by reverse reasoning, successful application of product development guarantees more efficient and fruitful research. With the discovery of a new chemical or with appreciation of a need for a chemical, a proper balance and close coordination between chemical research and market research must be maintained from the very beginning of the market development program (6).

History of Glyoxal

Consider the story of glyoxal—the first dialdehyde to be produced and sold on a commercial scale. It is the simplest dialdehyde, but its chemistry has fascinated research workers since its discovery. Although the chemistry of its synthesis is relatively simple, the skill of research chemists and process

engineers and the too often unrecognized genius of the production man were all required to make this chemical commercially available. In a few short years it has grown from a research photographic chemical selling for \$30.00 per pound to a full-fledged industrial raw material, used in approximately 50 different uses. From the bonding of cork sheet to the mothproofing of carpets, from the manufacture of disposable diapers to the embalming of cadavers (5)—literally from the cradle to the grave, glyoxal has found its way into many products which are integral parts of our daily life. The water-resistant match we carry in our pocket and the washable wallpaper on our living room also have probably been treated with glyoxal.

Glyoxal was originally synthesized by Debus (4) in 1856 and remained a curiosity on the laboratory shelf for almost 80 years thereafter. Then, in 1936, two chemists, R. W. McNamee and J. T. Dunn, of the research department of the Carbide and Carbon Chemicals Co., a division of Union Carbide and Carbon Corp., were requested to develop uses for ethylene glycol and its derivatives since it was then supposed there would be a great excess of

ethylene glycol, an eventuality that has not yet materialized. Since dehydrogenation reactions were an integral part of the company's operations, it was logical that the dehydrogenation of ethylene glycol should be attempted. Unfortunately in this instance, the dehydrogenation produced a bumper yield of hydroxymethyldioxolane and substantially no glyoxal. Oxidation, an older method of producing aldehydes from alcohols, was then tried and small yields of glyoxal were obtained. After a thorough investigation of such variables as temperature, pressure, catalysts, and structural materials for converter tubes, all of which were found to be of extreme importance, a process was developed which appeared commercially feasible (7).

The first sale of glyoxal was made to a photographic house in 1937. Shortly thereafter, because of its excellent reducing action, glyoxal was tested as a reducing agent for silver in the new and revolutionary Peacock Laboratories' spray process for applying silver to glass and plastic surfaces. This use was quickly patented by Peacock Laboratories (8). The first "large" customer for glyoxal was a pharmaceutical house which purchased substantial quantities of the sodium bisulfite addition product as an intermediate in the synthesis of pyrazine-2,3-dicarboxylic acid, an antipellagra vitamin similar structurally to nicotinic acid (2).

With a modest market established, a small pilot plant was built in the research department development unit at the Carbide and Carbon Chemicals plant at South Charleston, W. Va. This development unit, with a capacity of approximately 3 drums per month of an aqueous solution of glyoxal, provided glyoxal for all industrial development uses until the present commercial facilities were completed. In the meanwhile, Cluett, Peabody and Co. discovered that the treatment of spun viscose or cuprammonium rayon fabrics with glyoxal imparted a resistance to shrinkage which made the fabrics substantially shrinkproof even after 40 launderings. The size of this potential outlet for glyoxal and the possibility of expanding the range of uses for glyoxal, if it could be produced to sell at a much lower price, resulted in the decision to erect the larger facilities.

On completion of the new plant, which began operation in September 1946, a sales campaign to develop uses for glyoxal was begun. It was decided that glyoxal would be marketed in an aqueous solution with a minimum glyoxal content of 30%. Actually this solution is a mixture of monomeric and polymeric hydrates of glyoxal which in most chemical reactions behave as if the glyoxal monomer alone were present in the solution. Although the commercial solution contains significant amounts of ethylene glycol, formaldehyde, and formic acid as impurities (Table I), it had been amply demonstrated that the solution was as satisfactory for the treatment of rayon as a purer material. The belief that the aqueous solution would perform satisfactorily in other anticipated uses has also been confirmed.

TABLE I. PROPERTIES OF TECHNICAL GRADE, 30% GLYOXAL SOLUTION

pH of 30% solution at 20° C.	1.5-2.0
Specific gravity at 20°/20° C.	1.20-1.28
Color	Light yellow
Odor	Mild
Composition	% by Weight
Glyoxal (present in hydrated form)	30.0
Formaldehyde	3-7
Formic and glycollic acids	1-3
Ethylene glycol	6-15
Acetals	0.5
Water	Balance

Development of Applications

The major industrial applications for glyoxal utilize its ability to cross link both proteins and polyhydroxy materials. Glyoxal has a mild odor and a relatively low volatility in its aqueous solution; it does not irritate the skin or mucous membranes.

TABLE II. GLYOXAL INHIBITION OF IRON CORROSION

Pickling Inhibitor	% Inhibitor (by Weight)	Pickling Acid, % HCl	Exposure Time, Hours	Temp., ° C.	% Weight Loss of Iron ^a
Glyoxal	0.50	3.0	24	25	3.0
Formaldehyde	0.50	3.0	24	25	3.8
Blank	None	3.0	24	25	19.7
Glyoxal	0.10	3.0	24	25	5.1
Formaldehyde	0.10	3.0	24	25	7.3
Blank	None	3.0	24	25	19.7
Glyoxal	1.00	3.0	2.5	55-60	23.0
Formaldehyde	1.00	3.0	2.5	55-60	37.0
Blank	None	3.0	2.5	55-60	50.1
Glyoxal	1.00	1.0	25	25	0.6
Blank	None	1.0	25	25	7.7
Glyoxal	1.00	3.0	25	25	0.7
Blank	None	3.0	25	25	17.5
Glyoxal	1.00	5.0	25	25	14

^a In each test, 3,000 grams of iron, in form of small staples to provide maximum surface area, were exposed to 100 grams of solution contained in a standard 8-ounce jar.

These properties make it more suitable for some applications formerly served by formaldehyde, whose shortcomings along these lines are well known.

However, glyoxal is more than simply a replacement for formaldehyde; it has already struck out on its own. The Cluett, Peabody Sanforset process for the dimensional stabilization of rayon is a good example. Glyoxal's reactivity makes it a promising intermediate in the formation of resins, dyestuffs, pharmaceuticals, and other products. It can be reacted to form acetals, imidazoles, amines, the sodium bisulfite addition product, and phenylglycinanilide, an indigo intermediate. The future for glyoxal in the following uses appears particularly interesting:

1. The reaction product of 1 mole of glyoxal with 2 of urea, called acetylenediurein, looks very promising for creaseproofing textile fabrics. The intermediate is reacted with formaldehyde and additional glyoxal to give a permanent creaseproofing to cellulosic materials. This market for glyoxal may well be one of its largest in the near future.

2. Another of the more promising potential markets for glyoxal is in the wet strengthening of paper. The treatment of paper stocks such as paper toweling or saturating papers with glyoxal and Cellosize hydroxyethylcellulose increases the absorbency of the paper stock whereas a resin treatment actually causes a sharp decrease. Efficient and economic application of the glyoxal process to existing paper machines of the Fourdrinier type must still be attained, however.

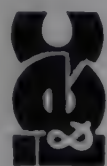
3. As a formaldehyde replacement, glyoxal is adaptable in such diverse uses as the preservation of histological species for laboratory study (11); as a hardening agent for photographic gelatin and gelatino-silver halide emulsions; as a spray to insolubilize the bonding agent for paper sheet from which lithographic paper and base paper for washable wallpapers are manufactured; and as an element in the formulation of deodorizers of the wick type.

4. A derivative of glyoxal and stearic acid amide greatly increases the water repellency of textile fabrics, particularly cellulosic fabrics, which are impregnated with the product (1).

5. The reducing action of glyoxal is responsible for its inhibition of corrosion of iron in the presence of aqueous hydrochloric acid (Table II). This reducing property of glyoxal is also the basis for one of its largest applications. It is used to reduce iron impurities in alumina catalysts to the ferrous state. The impurities are more soluble in the lower valence form and can more easily be washed out of the alumina to produce an "iron-free" grade, suitable as a petroleum cracking catalyst.

6. Resins formed by reacting glyoxal with ketones may be used alone or in combination with alkyd type resins for baking lacquers (9); resins prepared from glyoxal and *tert*-butyl cresol reduce interfacial tension between water and oil by as much as 25% when 2% of the condensation product is added (10); polyvinyl partial acetal resins when reacted with glyoxal are excellent knot sealers for preparing new wooden surfaces for painting (3).

As a cross-linking agent, glyoxal has a number of important uses in which it insolubilizes proteins and polyhydroxy materials.



PLANT PROCESS SERIES

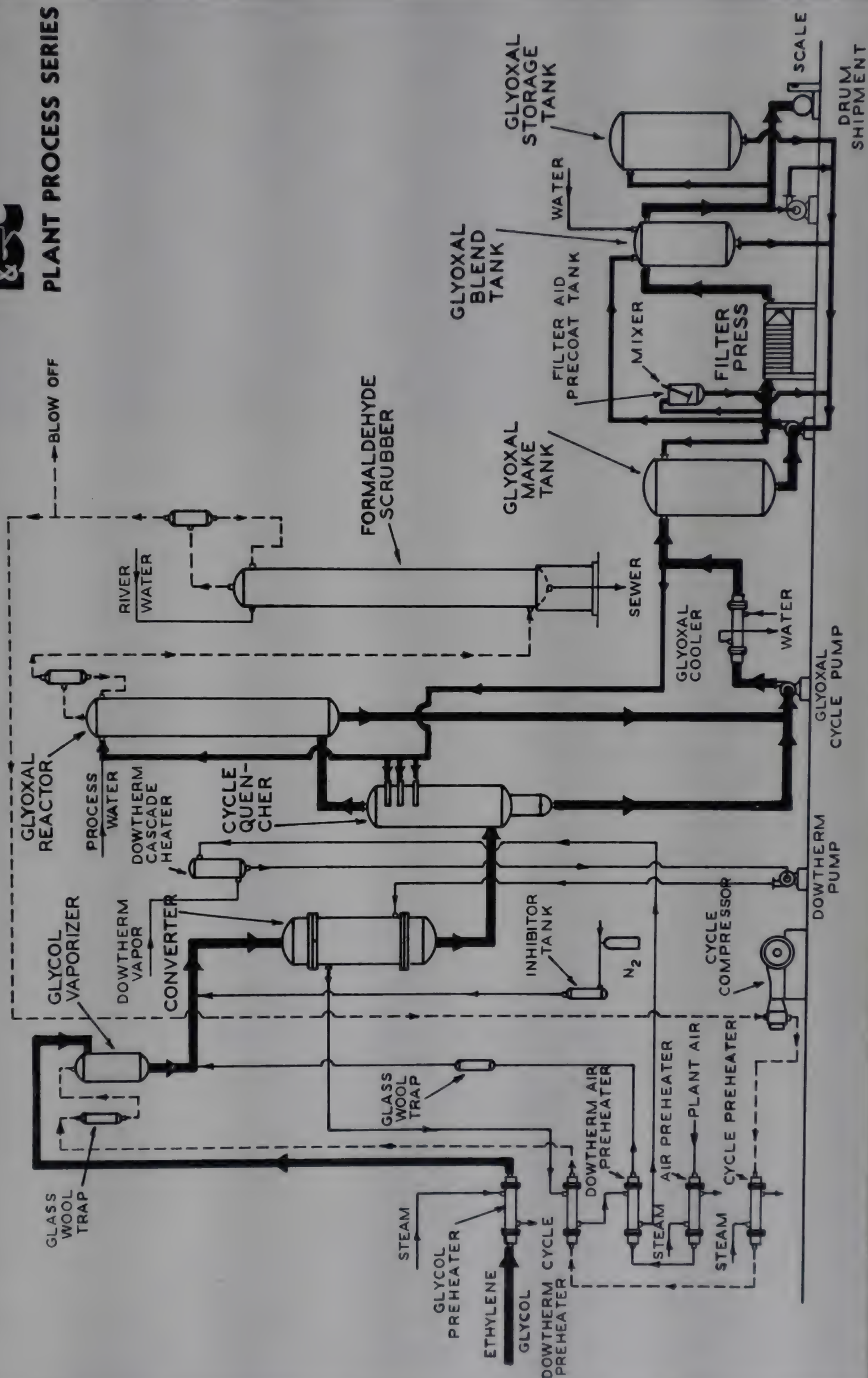


Figure 1. Flow Sheet for Production of Glyoxal at South Charleston, W. Va., Plant of Carbide and Carbon Co., a Division of Union Carbide and Carbon Corp.

Insolubilization of Proteins

The reaction of the two aldehyde groups in glyoxal with the amino and imino groups of a protein causes the protein molecules to cross link, making them partially or almost completely resistant to water. Glyoxal has been used commercially in a wide variety of applications including the manufacture of gaskets, water-resistant matches, washable wallpapers, and cork block and sheeting. In nearly all cases the desired result can be accomplished by mixing the protein and glyoxal, applying the mixture, drying, and heat curing it if necessary. The degree of insolubilization obtained varies with the conditions of reaction. In general, the more glyoxal used and the longer the heat cure or the higher the curing temperature, the more complete the insolubilization. For protein insolubilization, in general, from 1 to 3% by weight of contained glyoxal based on the protein solids is customary.

In general, this type of application may be followed through for all protein glues which require abnormally high water resistance. For example, washable wallpapers are prepared by spraying a glyoxal formulation on a printed wall paper which has been aftercoated with a protein. Special types of paper such as blueprint paper are sized with glue, then treated with glyoxal to permit usage under high humidity conditions.

Insolubilization of Polyhydroxy Materials

The insolubilization of polyhydroxy materials, such as starch, polyvinyl alcohol, and partially hydrolyzed polyvinyl acetate, is a cross-linking reaction similar to the insolubilization of proteins. In this case, however, glyoxal reacts with the hydroxyl groups of the material being insolubilized to form acetals or hemiacetals. The two materials are mixed, applied, and then subjected to a heat cure to drive off the water of reaction. In addition to those mentioned above, several typical materials that can be insolubilized by reaction with glyoxal are viscose or cuprammonium spun rayon, partial polyvinyl butyral resins, and Cellosize hydroxyethylcellulose.

Shrinkproofing rayon provides one of the major markets for glyoxal. Insolubilization of the rayon fibers is accomplished by padding a solution of glyoxal, about 4% by weight, on the cloth in the presence of acidic catalysts, after which the cloth is dried and cured. Fabrics treated in this way shrink less than 2% after forty launderings, yet the cloth does not become boardy and stiff. In addition, the treatment gives minimum chlorine retention, an improvement in dye fastness, and maximum resistance to shrinkage.

An important use for glyoxal results from its ability to react with starch and related substances, such as dextrin, to make them water resistant. For example, in the manufacture of envelopes, where dextrin adhesives are used for the closures, three problems arise—thickening of the dextrin solution on standing, curling of the paper coated with adhesive, and self-sealing of the finished closure under conditions of high humidity. The addition of approximately 3% by weight of commercial glyoxal based on the solids content of the dextrin solution overcomes these problems to a considerable extent. The dextrin solution viscosity remains stable on storage, the humidity resistance of the plasticized glue is high enough to prevent self-sealing even at 90% relative humidity, and sufficient plasticizer can be used to prevent curling of the paper.

Other applications in which glyoxal-modified starch adhesives are used include: the manufacture of paper boxes, such as soap powder boxes, which are liable to become wet during use; sealing cigarette papers; and affixing tax stamps or other labels to containers that may be subjected to high moisture conditions.



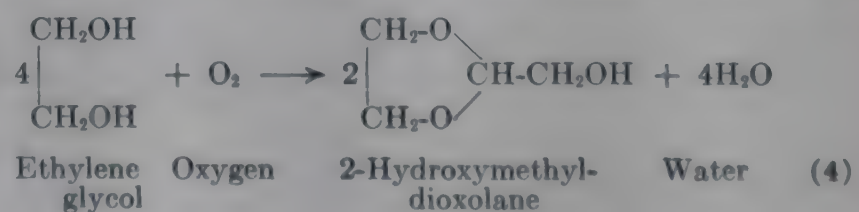
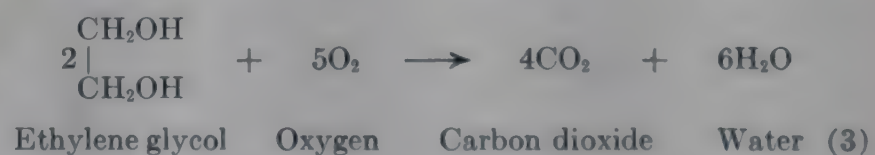
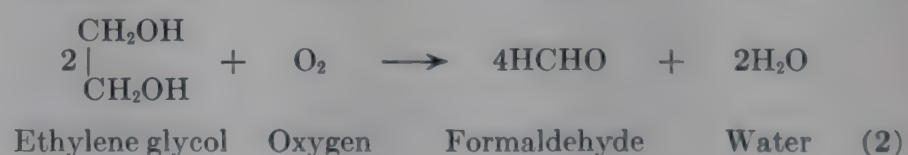
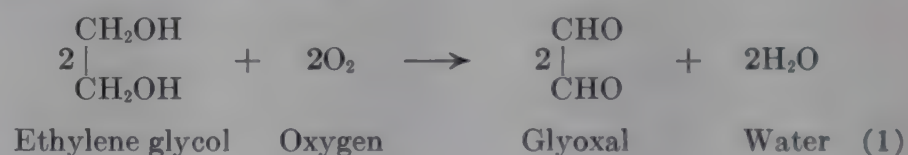
Glyoxal Tank Farm

Glyoxal is also used to modify starch in coating paperboard. Pigmented starch coatings can be made insoluble by a simple glyoxal treatment that yields a good water-resistant finish which will permit offset printing.

Glyoxal is an insolubilizing agent for partially hydrolyzed polyvinyl acetates and partial polyvinyl butyral resins. Five per cent of commercial glyoxal based on the dry weight of the polyvinyl acetate or of the butyral resins is added in normal commercial processes. Textile sizes prepared from polyvinyl acetate or polyvinyl alcohol can be made more water resistant under conditions of high humidity and elevated temperatures by the incorporation of 1 to 2% glyoxal in the sizing mixture. A cross-linked thermoplastic resin having excellent resistance to water and organic solvents is produced from the butyral resins. Sheets milled from this resin can be used for wrapping materials, insulating tape, raincoat materials, and for laminating glass, plywood, or metals.

Chemistry of Glyoxal Process

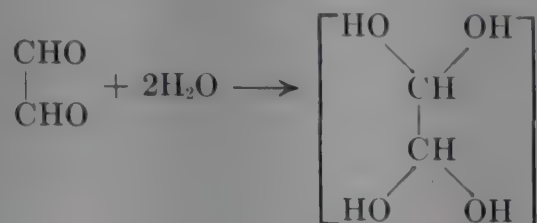
Glyoxal is manufactured commercially by the oxidation of ethylene glycol in the presence of a copper oxide catalyst. The reactions occurring in the catalytic zone are controlled by the quantity and type of inhibitor added and are influenced by the nature of the reaction tube.



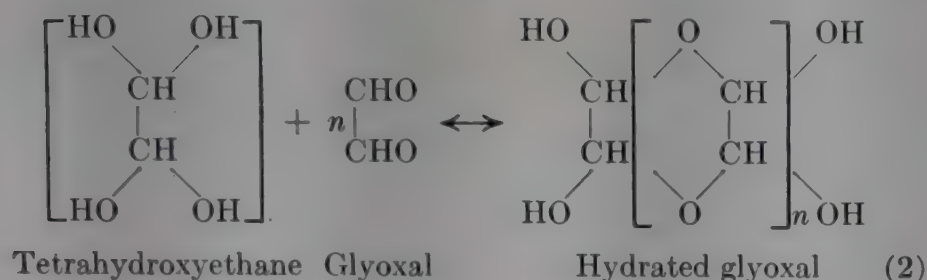
Reactions 2 and 3 are suppressed by the action of certain halogen compounds on the catalyst surface, thus making it possible to obtain a high ratio of glyoxal to formaldehyde with good ethylene glycol efficiency.

Reaction 4 occurs in the absence of oxygen or whenever a deficiency of oxygen is present. Under normal processing conditions 2-hydroxymethyldioxolane is not present in the product to an appreciable extent.

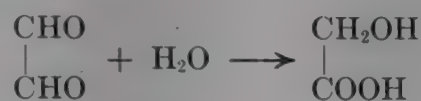
In the recovery system glyoxal is hydrated, reacting with water according to the following equations:



Glyoxal Water Tetrahydroxyethane (1)



Tetrahydroxyethane Glyoxal Hydrated glyoxal (2)



Glyoxal Water Glycollic acid (3)

Reactions 1 and 2 proceed very rapidly to yield an aqueous solution of hydrated glyoxal polymers. Reaction 2 is reversible. Accordingly, n in the equation has a value which depends on the concentration of glyoxal and which, for solutions up to 60%, lies between 1.0 and 3.5.

Reaction 3 occurs rather slowly in the recovery system. The resulting glycollic acid and a small amount of formic acid (the mechanism of its formation has not been clearly elucidated) make up the carboxylic acid impurities in technical glyoxal.

Manufacturing Process

The glyoxal unit of Carbide and Carbon Chemicals Co. is located on Blaine Island, South Charleston, W. Va., and has ready access to ethylene glycol raw material. A ground floor enclosed control room is centrally located, and the whole unit requires the services of only one operator per shift; he is stationed in the control room. The operator is responsible for the ethylene glycol feed tanks and glyoxal storage tanks located 35 feet away in a tank farm, and he also checks the operation of pumps and a compressor located in a room adjacent to the control room.

Aside from the inhibitor tank, which occupies a corner of the control room, all the major process equipment extends through two structural levels, a height of 35 feet. The glyoxal process is a vapor-phase cyclic system in which make-up air (the source of oxygen) and ethylene glycol are added to a more or less inert cycle containing nitrogen principally and some by-product carbon dioxide and unreacted oxygen. The use of an inert cycle permits addition of glycol and air to converter under controlled oxidation conditions and below the explosive concentrations of oxygen.

Plant Operation

Because the process is cyclic and continuous (Figure 1), normal plant operation, after start-up, involves control of flows of glycol, inhibitor, cycle gas, and air as well as temperature and pressure control. All are modified over rather narrow ranges (Table III) to obtain optimum glyoxal yields.

TABLE III. SUMMARY OF OPERATING CONDITIONS

Significant Point	Pressure, Lb./Sq. Inch	Temp., ° C.
Cycle compressor suction	14	4-30
Cycle discharge	23	48
Cycle after Dowtherm heat exchanger	22.5	280
Cycle at glass-wool trap	22	272-293
Cycle after ethylene glycol vaporizer	21	257-278
Inlet air	30	4-30
Inlet air after Dowtherm exchanger	21	256-277
Inhibitor tank	21.5	50-70
Inhibitor to converter inlet	21	110
Converter inlet	21	255-275
Dowtherm converter inlet	55	300-320
Converter outlet	17	305-325
Dowtherm converter outlet	53	304-324
Quencher outlet	16	35
Formaldehyde scrubber outlet	14.5	4-30
System pressure	14.5	4-30

A compressed cycle gas consisting of oxygen, carbon dioxide, and nitrogen passes through a steam and Dowtherm preheater and the cycle glass-wool trap. The trap is designed to remove all foreign matter causing side reactions. It is a Type 347 stainless steel vessel (26 inches in diameter by 7 feet 4 inches long) equipped with a Type 347 stainless steel basket, 12-inch inside diameter and 20-inch outside diameter, which extends down into the vessel for 4 feet and is filled in the annular space with glass wool. Design maximum operating pressure of the vessel is 50 pounds per square inch.

Ethylene glycol is vaporized by spraying liquid glycol, preheated to 275° C., into the cycle gas stream near the top of the glycol vaporizer (Figure 2) from a set of six stainless steel 1/8-inch opening spray nozzles. The sprays direct the glycol into concurrent flow with the cycle gas. The glycol vaporizer is a packed, Type 347 stainless steel vessel 3 feet in diameter and 6 feet long, and has a designed working pressure of 50 pounds per square inch. The packing consists of 2 feet of 1.5-inch porcelain Raschig rings with 1 foot of 1-inch rings above the larger ones. There is no grating separating these rings. Plant air, which has been preheated with steam and Dowtherm, is added to the effluent gas from the ethylene glycol vaporizer. The inhibitor tank, an insulated vessel 12 inches in diameter by 48 inches high, has a capacity of 20 gallons and is located in the control room of the

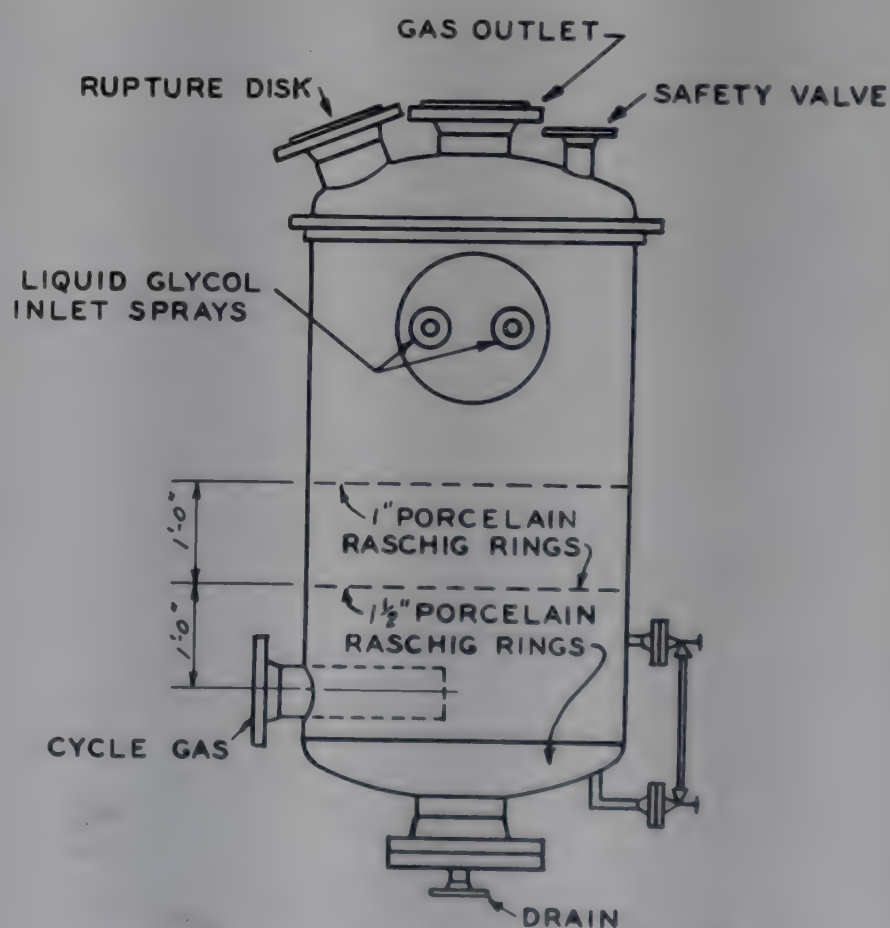


Figure 2. Ethylene Glycol Vaporizer

glyoxal unit. The vessel (Figure 3) is equipped with four nozzles, located around the vessel near the bottom, and gage glass connection. A controlled nitrogen flow enters one of the nozzles through a 1-inch drilled steel sparger pipe. A small steam coil of copper is placed in the second nozzle, and a recording thermometer well is placed in another connection in order to control the temperature of the contents of the vessel by control of steam. A small steel pot is connected to the top of the inhibitor tank for charging the inhibitor during operation.

The inhibitor flow, consisting of about 50 to 70 cubic feet per hour of nitrogen laden with the halogen inhibitor is added to the converter inlet gases at the shortest distance from the converter inlet that still allows thorough mixing. In the converter, 80 to 85% of the ethylene glycol is converted to the various oxidation products consisting of glyoxal, formic acid, formaldehyde, carbon dioxide, and water.

The converter (Figure 4) consists of a shell-and-tube heat exchanger; over-all dimensions are: diameter 5 feet and length 14 feet 2 inches. There are 745 tubes, each 10 feet long (1.03-inch inside diameter and 1.25-inch outside diameter) made of Hastelloy alloy B and supported on each end by steel tube sheets clad on the tube side with $\frac{3}{16}$ -inch Hastelloy alloy B. The top head is clad on the inside with $\frac{3}{16}$ -inch Hastelloy alloy B and the bottom head is equipped with a false bottom which lies beneath the bottom tube sheet and is connected to the outlet nozzle. This false bottom is constructed of Hastelloy alloy B. The top and bottom tube sheets are covered by 8-mesh Hastelloy alloy B screens which are held in place by a 1-inch mesh Hastelloy alloy B grating. The designed working pressure of this equipment is 150 pounds per square inch at 650° F.

The catalyst which is charged into each tube of the converter consists of a 9.5-foot section of 2 × 4 mesh Aloxit impregnated with copper nitrate to yield, after roasting, an oxide with a copper content of 3 to 8%. The catalyst section occupies the inside tube area of the 745 Hastelloy alloy B tubes. The total catalyst volume is approximately 40 cubic feet. A single batch of catalyst is used a year or more and is regenerated infrequently.

The converter outlet gases are quenched by cooled glyoxal quencher liquid as quickly as possible after leaving the converter (Figure 1). Liquid flow to the quencher is 140 gallons per minute. The hot gases leaving the converter are quenched quickly rather than heat-exchanged because there is a tendency for glyoxal to decompose at high temperatures; also, as glyoxal reaches the dew point it has a tendency to combine with small amounts of water to form a hard, horny polymer. The cycle quencher consists of a tower (4 feet in diameter by 13 feet, 7 inches high) of Type 347 stainless steel equipped in the top part with a series of three 2-inch spray nozzles having a capacity of 140 gal-

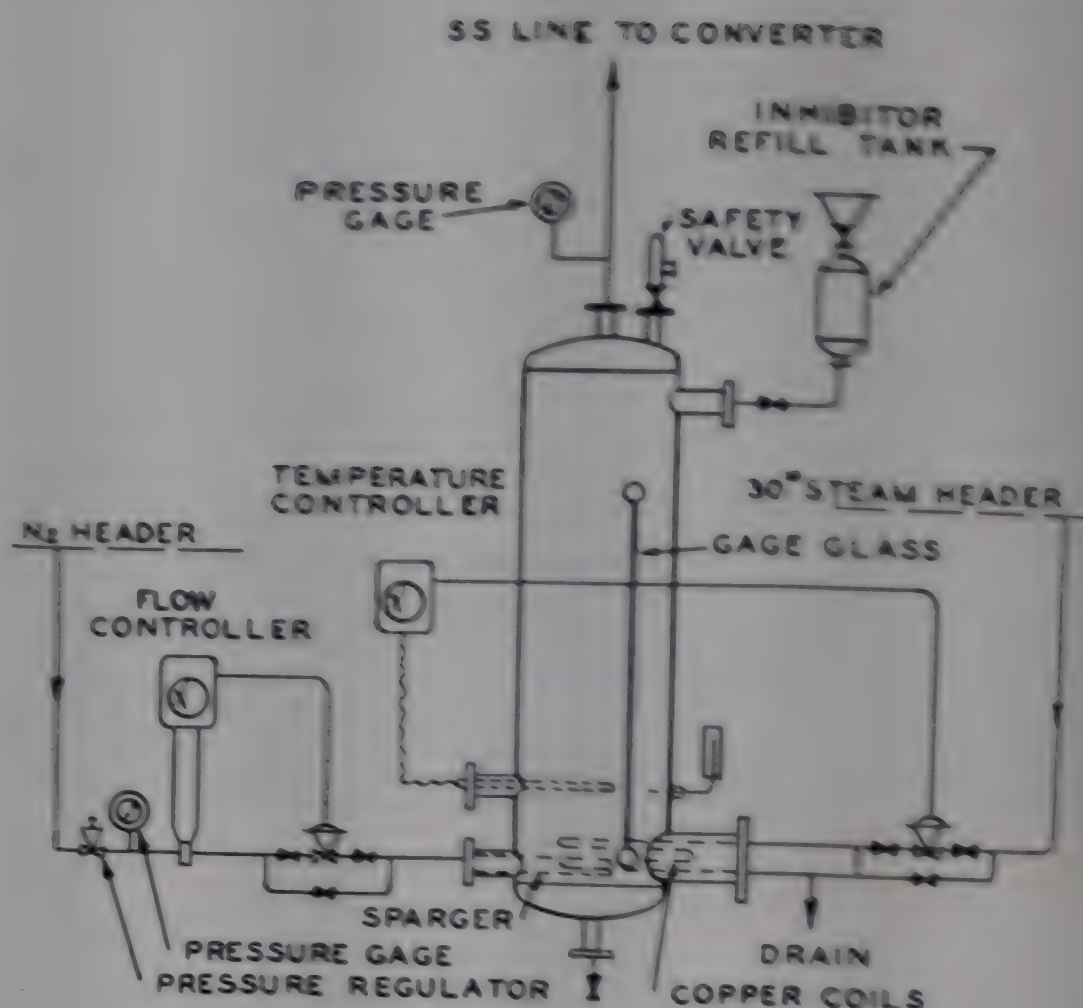
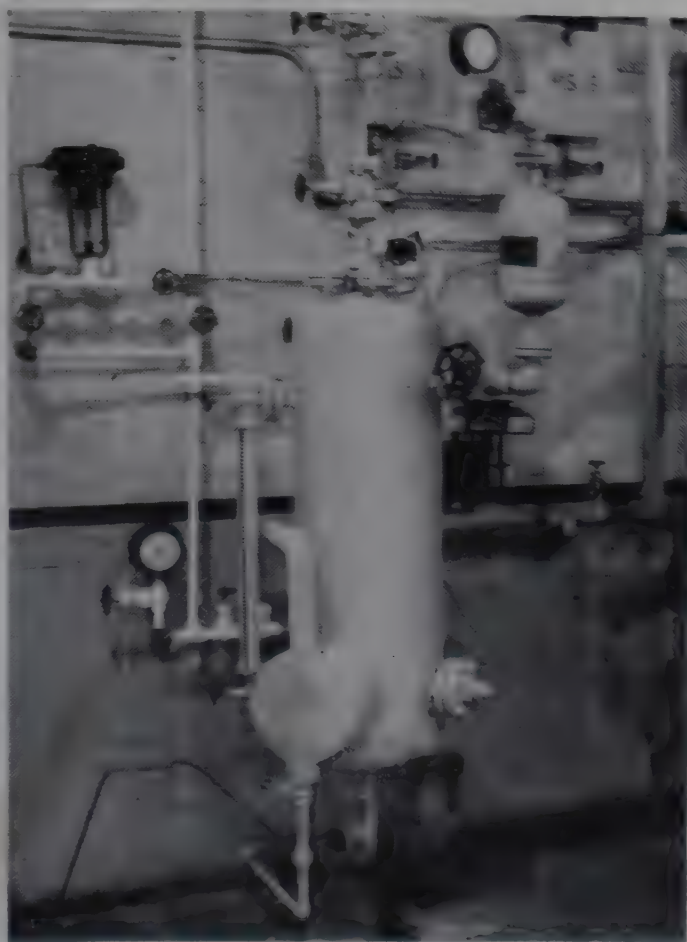


Figure 3. Glyoxal Inhibitor System

lons per minute. The hot gases from the converter enter the bottom of this vessel and flow countercurrent to the liquid flow. This vessel has a designed working pressure of 50 pounds per square inch.

From the quencher, the cycle gas is passed through the glyoxal reactor, a packed column where further contact is made with glyoxal quencher liquid. Thus any gaseous glyoxal is reacted with water in the glyoxal solution. Flow of liquid to the reactor is 20 gallons per minute. The reactor consists of a 25-foot tower, 4 feet in diameter and packed with 20 feet of $1\frac{1}{2}$ -inch porcelain Raschig rings; it is constructed throughout of Type 347 stainless steel. The cycle gases, which have been previously quenched, are passed up through this column and cooled quencher liquid is passed down through the rings to obtain contact of liquid and gas. The designed working pressure of this vessel is 50 pounds per square inch.

In the quencher and reactor, a large part of the reaction products and unreacted ethylene glycol are condensed to make a 32% glyoxal solution. In order to keep the glyoxal solution at 32% concentration, process water is added to the liquid cycle to augment the water of reaction formed in the converter. The level of the quencher cycle is controlled by a liquid-level differential controller, and the excess 32% solution is pumped off to the glyoxal make tank. There is a total production of 227 pounds per hour of solution having a composition of 32% glyoxal, 12.8%



Inhibitor System

TABLE IV—INSTRUMENT CONTROLS

Name	Type Instrument	Operation
East Panel (Reaction)		
Recorder, cycle flow	Flow controller	Motor valve in steam line to compressor sounds alarm, shuts off motor valve on inlet air and inlet glycol lines in event of low cycle
Indicator, low cycle flow	Flow controller	
Recorder, inlet air flow	Flow controller	Motor valve in plant air line
Recorder, inlet glycol flow	Flow controller	Motor valve in inlet glycol feed line
Indicator, Dowtherm flow	Flow controller	Alarm for low Dowtherm flow
Recorder, converter inlet pressure	Pressure controller	Sounds high pressure alarm and shuts off inlet air and glycol
Recorder, inhibitor flow	Flow controller	Motor valve in inlet nitrogen line to inhibitor tank
Recorder, inhibitor temperature	Temperature controller	Controls temperature of inhibitor tank by control of steam to coil
Recorder, oxygen analyzer		Shows record of oxygen content of converter inlet gas
Indicator, converter inlet pressure	Dial gage	Converter inlet pressure
Indicator, converter outlet pressure	Dial gage	Converter outlet pressure
Recorder, Dowtherm circulating temperature	Temperature controller	Controls circulating Dowtherm temperature by operating motor valve on Dowtherm inlet vapor or motor valve on water to Dowtherm cooler
Indicator potentiometer	...	Indicates eight temperatures throughout converter system
West Panel (Recovery)		
Recorder, water flow to reactor	Flow controller	Records flow of make-up water to glyoxal reactor to hold glyoxal concentration at 32%
Recorder, temperature of glyoxal cycle	Temperature controller	Records liquid cycle temperature and sounds high temperature alarm
Indicator, glyoxal liquid cycle liquid level	Differential controller	Controls level in liquid-level tank by taking off make from cycle to glyoxal make tank by motor valve setting
Recorder, water flow to formaldehyde scrubber	Differential controller	Sounds alarm in event of high column differential
Indicator, formaldehyde scrubber liquid level	Differential controller	Controls river water level in base of column and high level sounds alarm
Recorder, system pressure	Pressure controller	Controls pressure of system by regulating blow-off
Recorder, system blow-off	Orifice meter	Shows amount of blow-off from unit

unreacted glycol, 5.9% formaldehyde, 1.6% glycollic acid, and 0.32% formic acid. The glycollic acid is formed by the reaction of glyoxal and water in the quencher cycle. The remainder of the cycle gases, which are now devoid of the condensable products, is passed through the formaldehyde scrubber (a packed column with a flow of 3000 gallons per hour of river water) where the formaldehyde is scrubbed from the cycle gas to eliminate formation of formaldehyde polymer in the cycle compressor. The formaldehyde scrubber consists of a 42-inch diameter column, 31 feet high, packed with a 20-foot section of 1-inch porcelain Raschig rings; the column is constructed of Type 347 stainless steel clad on steel and has a designed working pressure of 50 pounds per square inch.

The blowoff of cycle gas from the system is taken from the top of the formaldehyde scrubber, and the rest of the cycle is returned to the cycle compressor, where it is recompressed and again cycled through the system.

The glyoxal solution in the blend tank is diluted with process

water to make a 30% solution and is filtered, blended, and drummed.

Instrumentation

The glyoxal unit is operated on a continuous basis, and all conditions in normal operation are relatively constant (Table III).

The instrumentation of the glyoxal unit is highly centralized in the control room. With the exception of the gages on the ethylene glycol feed tanks and glyoxal make and storage tanks, which are located at the base of each tank, and the quencher and reactor liquid flowmeters located on the ground level of the equipment, the air-actuated controls are situated on the east reaction panel and west recovery panel in the control room. Also located in the end of the control room between the panels is the alarm panel which indicates individual equipment failure in event of an emergency.

Materials of Construction

In the design of the glyoxal unit there are three situations which require the use of stainless steel or other special alloys. First, ethylene glycol vapor at elevated temperatures in the presence of oxygen has a tendency to decompose to formaldehyde. This tendency, accelerated by the presence of iron in the system, is minimized by Type 347 stainless steel. Therefore, the equipment on the converter inlet is constructed of Type 347 stainless steel for a short distance preceding the ethylene glycol entry to the converter. So that no iron is carried into this part of the system from the preceding steel equipment, glass-wool traps are installed on the cycle flow line and in the inlet air line, and cotton-packed screen filters are installed on the inlet glycol line to the vaporizer. All piping, valves, and equipment between these glass-wool traps and filters and the converter inlet are constructed of Type 347 stainless steel. Secondly, glyoxal in the vapor phase in the converter has a marked tendency to decompose to formaldehyde. This decomposition is extreme in the presence of iron; it is less in the presence of stainless steel; and it is least in the presence of Hastelloy alloy B. Therefore, the converter tubes and the inside of the heads and tube sheets of the converter in contact with glyoxal are constructed of this special alloy. Because glyoxal is very reactive in the vapor phase in the presence of oxygen and has a tendency to form a horny polymer in the presence of minute quantities of liquid water, the converter outlet gases are quenched as quickly as possible in the liquid quencher. Since the line from the converter outlet to the quencher is short, Type 347 stainless steel is satisfactory for this service.

Thirdly, Type 347 stainless steel is required in the quencher cycle because the glyoxal solution contains 0.2 to 0.6% formic acid, which is very corrosive to ordinary steel. The entire quencher and reactor cycle, consisting of quencher, reactor, quencher cycle pumps, cooler, valves, and piping, is constructed of Type 347 stainless steel. Also, the glyoxal make and storage tanks, miscellaneous lines, and valves are constructed of this type stainless steel for the same reason. Since traces of formic acid are carried into the formaldehyde scrubber in the gas stream, this vessel is constructed of Type 347 stainless steel clad on steel to resist the corrosion. The remainder of the cycle piping back to the glass-wool trap is constructed of ordinary steel and the same material is used for the compressor and heat exchanger. The inlet ethylene glycol system as far as the filter, the inlet air system as far as the glass-wool trap, and the inhibitor system as far as the outlet vapor line are all constructed of ordinary steel with conventional type valves. The Dowtherm circulating system is made of the steel piping and steel pumps and valves normally recommended for this service by the Dow Chemical Co.

The ethylene glycol feed pumps, one for operation and one spare, are turbine pumps having a capacity of 2 gallons per minute and a discharge pressure of 75 pounds per square inch.

These pumps are constructed of steel with no special parts. Since the ethylene glycol used in the process is regular shipable grade material and contains no abrasive materials, these pumps have operated satisfactorily with little maintenance.

The Dowtherm circulating pump and a spare are regular 200-gallon-per-minute centrifugal cast steel pumps recommended by the Dow Chemical Co. for this service. These pumps are shop packed with high temperature packing.

The glyoxal quencher cycle pumps, one for operation and one spare, are 200-gallon-per-minute, 100-foot head centrifugal pumps constructed throughout of Type 347 stainless steel and related alloys. These pumps are single stage, equipped with a mechanical seal, and a closed type impeller.

The glyoxal transfer pump located in the tank farm for transfer of glyoxal is similar in construction to the quencher cycle pumps. Since these pumps are not in continuous service, a regular rope asbestos packing is normally used.

Safety

The glyoxal process was planned with the intention of protecting the operating personnel from injury and the equipment from overpressure. Since the equipment was designed for operation by one operator, the control unit for this and another process unit were put in the same room so the operator would have a companion operator working with him. The operating equipment was located almost entirely in the adjacent outside structure in order to avoid concentrations of explosive mixtures. The unit was instrumented and operated from a control room closed off from the equipment; thus, the operator normally would not be near the equipment for any long period.

The equipment is protected from excessive pressure by rupture disks and safety valves. Stainless steel rupture disks, 8 inches in diameter, are placed on the reaction system at the top of the ethylene glycol vaporizer and at the top of the converter. Safety

valves are located on the reaction system at the top of the ethylene glycol vaporizer and the converter, between the glyoxal quencher and reactor, at the top of the formaldehyde scrubber, and on the discharge of the cycle compressor. These valves, constructed of steel body and stainless steel parts, have 4-inch discharge connections and are set to relieve at 50 pounds per square inch. Safety valves are also located on the Dowtherm system at the top of the converter shell and at the top of the Dowtherm cascade heater. These valves are constructed of steel with 3-inch discharge connections and are set to relieve at 100 pounds per square inch pressure. The glyoxal make and storage tanks are each equipped with safety valves which have a 4-inch discharge connection and are constructed of steel with stainless steel seats. The tank safety valves are set to relieve at 30 pounds per square inch pressure. The ethylene glycol tanks have no safety valves because they are vented to the air with no valves in line.

Quality Control

The converter inlet and cycle gas samples are taken off the converter inlet line near the converter and off the cycle line after the cycle compressor. Reducing regulators are installed immediately after the sample connections in each line to reduce the sample gas to near atmospheric pressure. After the regulators, the continuous sample is run through $\frac{1}{4}$ -inch copper tubes to the Orsat analyzers in the control room. The regulators are adjusted to allow bubbling of a continuous sample into 4 inches of water in a bottle located on the floor of the control room. The analyzer sample connections on the sample lines are taken off before the gas reaches the bubble bottle. Orsat analyses for carbon dioxide and oxygen are run each half hour on the converter inlet and each hour on the cycle gas.

A sample line similar to the ones described above is run to the oxygen continuous analyzer from the converter inlet line.



Reaction Panel Board, Inhibitor Tank, and Orsat Machine in Control Room



Drum-Loading Room

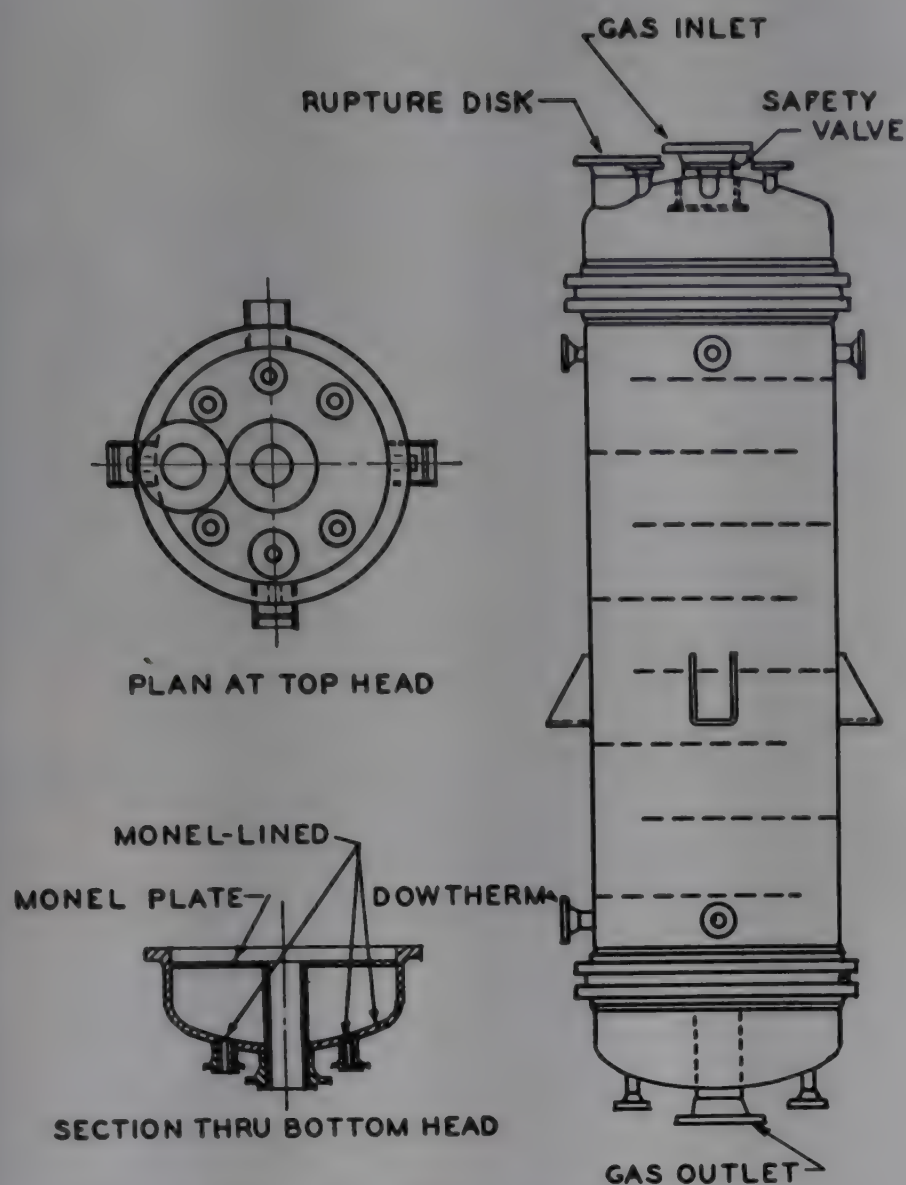


Figure 4. Glyoxal Plant Converter

The other sample taken during regular operation is an hourly check of the specific gravity of the glyoxal quencher cycle. An empirical chart has been plotted to show specific gravity versus glyoxal concentration. These samples are taken from the discharge of the quencher cycle pump on the east side of the control room in a 500-ml. specific gravity container and are brought into the control room and cooled to 20° C. After the gravity is taken, 100 ml. of the sample are placed in a 1-gallon jug to make up a 24-hour composite. The remainder of the sample is placed in a drum and ultimately pumped into the glyoxal make tank.

A sample of the glyoxal quencher composite, and a 7:00 A.M. quencher cycle spot sample are sent each day to the control laboratory for complete analysis, which consists of determination of the glyoxal, ethylene glycol, glycollic acid, formic acid, and formaldehyde content. Analyses of these samples form the basis for operating control of product composition. Indicator titrations are used for the determination of glycollic acid, formic acid, and glyoxal, in that order. As glyoxal interferes in the formaldehyde titrations and in the ethylene glycol determination, it is factored from the apparent results of each titration.

The laboratory personnel run samples of the blend tank from time to time. The sample is taken after the tank has been circulated for 4 to 6 hours. Since the glyoxal is sold as a 30% solution and since the quencher cycle is normally operated at 32% concentration, it is necessary to dilute the solution with water to arrive at correct concentrations. The works laboratory personnel run samples of the blends after a tank has been circulated for 6 hours.

The laboratory personnel run the final samples for shipment, and these are also taken directly from the drum-loading line and are checked by the shipments laboratory.

Process Economics

Capacity of the glyoxal unit is 5800 pounds per day of 30% solution. Practical efficiency of the operation is approximately

40%, and chemical efficiency is 50 to 60% with unreacted ethylene glycol remaining in the glyoxal solution.

The unit is operated on a 24-hour basis by three shifts working 8 hours per day each. The operators work a 5-day week; thus 4 $\frac{1}{6}$ operators cover a week of 21 shifts. Supervision requires the part-time services of a chief operator, foreman, department head, and technical assistant for an aggregate manpower of 2 $\frac{1}{2}$. Laboratory work is performed by one technician, or an equivalent manpower of 1 $\frac{2}{5}$ for service 7 days per week. In all, then, 8.1 men function full or part-time in the unit.

Utility requirements are as follows:

1. Steam	Lb./Hour
(a) 180 lb./sq. inch for gas preheating, condensing	450
(b) 180 lb./sq. inch to 30 lb./sq. inch steam gas compression	1400
Total	1850
2. Electric power	Kw.
(a) Quencher cycle pump	12.4
(b) Dowtherm circulating pump	12.4
(c) Glyoxal transfer pump	12.4
(d) Heat for Dowtherm vaporizer	120.0
Total	157.2
3. River water	Gal./Min.
(a) Formaldehyde scrubber flow	50
(b) Quencher cycle water	100
Total	150

A calculation of glyoxal economics from these data must yield the conclusion that glyoxal has been priced to offer fullest encouragement for potential applications. And as demand unfolds, larger production volumes and, thus, lower unit cost will satisfy the requirement necessary to Carbide's existence—making a profit on an investment. Completion of the development cycle, beginning with research, advancing through commercial product and product use development, and ending with a profitable operation, will then be achieved.

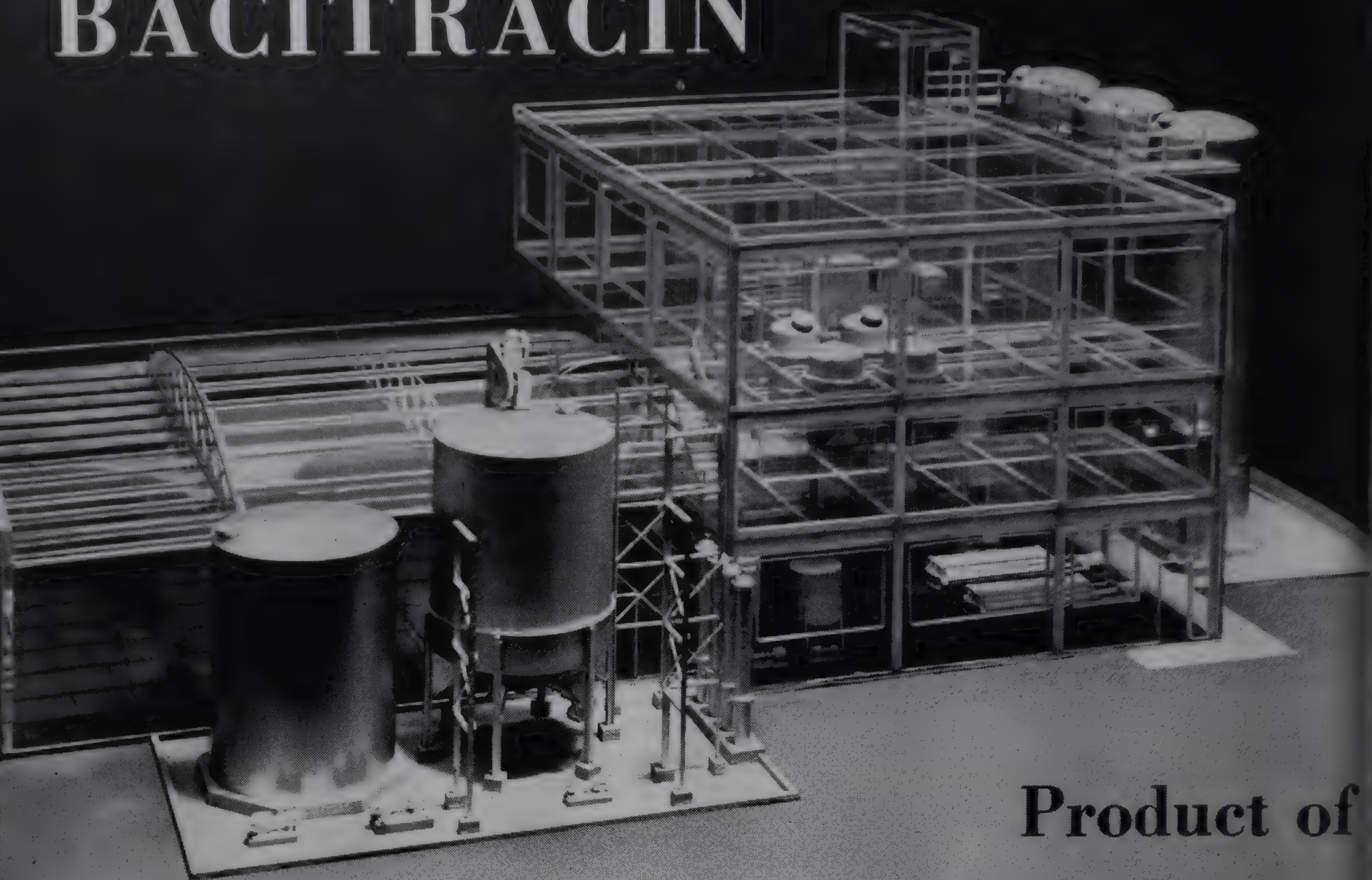
Future Prospects

The annual production of glyoxal has not been large in comparison to such chemicals as alcohol or acetic anhydride, but sales have increased steadily since the plant was placed in operation. Because markets for the new chemical are increasing and current sales requirements already exceed the plant capacity, Carbide and Carbon Chemicals are now planning a plant expansion. Glyoxal is emerging from its chemical adolescence and its growth rate is quickening. The larger scale facilities will permit more economical production, and this in turn will open new markets. Glyoxal, thanks to the ingenuity and cooperative endeavor of a smooth working team of research, development, production, and sales is taking its place as an industrial chemical.

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BACITRACIN



Product of Biochemical Engineering

Scale Model of Commercial Solvent's Bacitracin Plant, Terre Haute, Ind.

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DURING the past several years the production of antibiotics has been one of the prime reasons for an amazing growth of the pharmaceutical industry. Penicillin was the forerunner of this new group of pharmaceuticals, but it was soon followed by streptomycin and such newer antibiotics as aureomycin, chloramphenicol, terramycin, and bacitracin. The tremendous increase in the production rates of penicillin and streptomycin in this country is shown by Table I. The newer antibiotics in most cases are produced primarily by one manufacturer, and for this reason individual production rates are not available.

Bacillus subtilis and related bacteria of the Gram-positive spore-forming rod type produce a variety of antibiotics. A comparison of the most noteworthy shows that many are polypeptides or at least are large molecules which yield amino acids on hydrolysis. Some of the better known of these are listed in Table II.

Random isolations of spore-forming aerobes from soil give a surprising proportion that produces antibiotic substances. Those listed in Table II are only a small portion of the total. The

problem for the investigator is to find one with relatively low toxicity for animals and high toxicity for microorganisms.

However, the organism that produces bacitracin was discovered not in the soil but in a culture taken from an infected wound. This was in 1943; Margaret Tracy (then seven years old) recovered from a dirt-contaminated compound fracture of her leg after signs of infection had suddenly disappeared. In following the course of her recovery, Johnson, Anker, and Meleney (8) isolated a strain of *Bacillus subtilis* from the wound, and from this they were able to produce the new antibiotic which they called "bacitracin" in honor of the young patient. Filtrates of cultures of this bacterium were found to be bacteriostatic to a variety of Gram-positive bacteria, particularly the cocci.

A discussion of the laboratory methods of bacitracin production, concentration, and partial purification with a summary of the properties of the crude product was prepared by Anker *et al.* (1). Craig *et al.* (4) reported on purity studies made on bacitracin and the pharmacological characteristics of the antibiotic were brought out in papers by Scudi, Coret, and Antopol (13, 14). Some of the early tests of bacitracin on rabbits were described by

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Eagle and his coworkers (5-7). Meleney and Johnson (10) published a paper describing the first one hundred cases of surgical infections treated topically with bacitracin.

CHEMICAL AND PHYSICAL PROPERTIES OF BACITRACIN

Bacitracin as it is currently produced commercially is a light-gray hygroscopic powder with a bitter taste. Its purity, in terms of the arbitrarily defined unit, is approximately 45 units per milligram. According to Craig (4) maximum activity of pure bacitracin is 60 units per milligram.

Although the exact chemical structure of bacitracin is not known, elementary analysis reveals carbon, hydrogen, nitrogen, and sulfur but no halogen or phosphorus. Molecular weight determinations using the spread film technique have given values of 2700 if the substance is a monomer and 5400 if it is a dimer. Acid hydrolysis of bacitracin produces amino acids; approximately 90% of the total nitrogen is present as amino nitrogen. The composition of typical bacitracin preparations compared with a typical protein is shown in Table III.

Bacitracin resists hydrolysis by pepsin and trypsin and a variety of other proteolytic enzymes. It is, however, readily hydrolyzed by strongly acidic or basic solutions, particularly when heated. It is readily soluble in water; 1 gram of bacitracin will dissolve in 1 ml. of water at room temperature. Solubility in other solvents is summarized in Table IV.

Because of the complexity of the molecule, there are no absolute methods for determining the concentration of bacitracin solutions (referred to as the titer); usually the growth-inhibiting properties of an unknown are compared with those of a known or control sample. One unit of bacitracin has been arbitrarily defined as the amount which, when diluted 1 to 1024 under specified serial dilution assay conditions, completely inhibits the growth of a specific strain of group A hemolytic streptococcus (1).

In practice, bacitracin is assayed by means of a plate assay method using *Micrococcus flavus* as the test organism. Petri dishes are poured with nutrient agar and seeded with a thin layer of agar containing the test organism. Six stainless steel cylinders are dropped by means of a special positioning device onto each plate after the agar has solidified. Dilutions of the unknown containing approximately 1 unit of bacitracin per ml. are introduced into each of three cylinders. Into the other three a standard bacitracin solution containing 1 unit per ml. is placed. After incubation overnight the test bacteria grow except where the bacitracin has diffused through the agar giving a zone of no growth where the bacteria are inhibited by the antibiotic.

The diameter of this zone is proportional to the concentration of bacitracin in the unknown. The zones are measured and compared with the standard. The assays are read from a curve which has been established by a series of dilutions of standard.

One of the outstanding properties of bacitracin when compared with other antibiotics is its relative stability. After refluxing in aqueous solution of bacitracin at 100° C. for 30 minutes, 85% of its activity is still retained. Bacitracin solutions appear to be most stable in the pH range 4 to 5. The effect of pH on the stability of bacitracin in buffer solution is shown in Table V.

Bacitracin, in the dried state in vacuum vials, is stable at room temperature almost indefinitely. Even at 100° C., 83% of the activity of the dried product is retained after 24 hours.

FORMULATIONS AND THERAPEUTIC VALUE

At the present time, bacitracin is not generally recommended for intramuscular or intravenous injection (11, 12). It is available in ointments, nasal solutions, oral tablets, troches, and powder for the preparation of solutions.

The antibacterial properties of bacitracin, in general, are quite similar to those of penicillin. It is predominantly active against Gram-positive pathogens, including the common streptococci and staphylococci. Resistant strains do not develop rapidly and allergic reactions are quite uncommon. It is this relative freedom from allergic response that has made bacitracin one of the

TABLE I. DOMESTIC PRODUCTION OF PENICILLIN AND STREPTOMYCIN

	Production (Including Salts and Derivatives), Kilograms	
	Penicillin ^a	Streptomycin
1945	4,231	3
1946	15,485	1,132
1947	24,856	9,687
1948	57,513	37,709
1949	79,937	83,699
1950 (Est.)	133,383	92,446

^a Figures supplied by U. S. Department of Commerce, converted to kilograms by assuming 0.6 microgram per unit for penicillin.

TABLE II. ANTIBIOTICS PRODUCED BY *Bacillus subtilis* AND RELATED ORGANISMS

Antibiotic	Producing Organism
Bacitracin	<i>Bacillus subtilis</i>
Bacillin	
Eumycin	
Subtilin	
Tyrocidin	<i>Bacillus brevis</i>
Gramicidin	
Gramicidin S	
Colistatin	<i>Bacillus sp.</i> <i>Bacillus circulans</i> <i>Bacillus licheniformis</i> <i>Bacillus simplex</i>
Circulin	
Licheniformin	
Simplexin	

most important of the antibiotics to dermatologists. Furuncles, carbuncles, sties, and impetigo have all been treated successfully by topical application.

When mixtures of penicillin and bacitracin are used a synergistic action rather than merely an additive effect is observed (2, 6). The synergistic effect varies depending on the organism encountered; it is very dramatic with some cultures, less pronounced with others.

LABORATORY PRODUCTION

The primary requirement for a medium producing high titers of bacitracin is a high concentration of a plant protein such as soy-

TABLE III. ELEMENTARY ANALYSES OF BACITRACIN COMPARED WITH A TYPICAL PROTEIN

	Bacitracin	Protein
Carbon, %	50.0-52.0	51.0-55.0
Hydrogen, %	7.3-7.5	6.5-7.3
Nitrogen, %	13.7-14.7	15.5-18.8
Sulfur, %	1.9-2.3	0.3-2.2

TABLE IV. RELATIVE SOLUBILITY OF BACITRACIN IN VARIOUS SOLVENTS

rs = readily soluble s = soluble		ss = slightly soluble ns = insoluble	
Water	rs	Pyridine	ss
Methanol	s	Acetone	ns
Ethyl alcohol (abs.)	s	Acetonitrile	ns
n-Propyl alcohol	ss	Petroleum ether	ns
Isopropyl alcohol	ss	Benzene	ns
n-Butyl alcohol	ss	Nitromethane	ns
sec-Butyl alcohol	ss	Chloroform	ns
tert-Butyl alcohol	ss	Ethyl acetate	ns

TABLE V. EFFECT OF pH ON STABILITY OF BACITRACIN IN BUFFER SOLUTION

pH	Per Cent Retained Activity After		
	23 hours	71 hours	120 hours
2.4	58	37	18
4.4	94	88	70
5.9	90	73	45 ^a
7.9	88	56	31 ^a
9.0	80	27	27

^a 143-hour values.



Bacitracin Culture Transfer "Coop" Is Equipped with Germicidal Lamps

bean meal. A small amount of carbohydrate is required with soybean meal to prevent excessive deamination of the proteins and early development of a high pH.

The conditions of an air-agitated plant scale fermentor are approached in the laboratory by use of a cotton-plugged Erlenmeyer flask on a shaker. The shaker is a four-wheeled table with a lateral reciprocating motion furnished by an electric motor. The cotton plug allows air to mix with the media but filters out possible contaminants. Changes in air rates can be simulated by changing the ratio of the volume of the flask to the volume of the medium.

The bacitracin titers in representative media attained by the shake-flask technique are shown in Table VI.

TABLE VI. BACITRACIN PRODUCTION IN VARIOUS MEDIA

Main Nutrient in Medium	Peak Titer of Bacitracin, Units/Ml.
Peanut granules	71
Soybean meal	65
Lima bean meal	50
Soybean digest	45
Cottonseed meal	35
Swift's protein hydrolyzate	10
Casein digest and beef extract	2

Bacitracin was produced by Johnson, Anker, and Meleney (8) in static surface culture on a synthetic medium composed of glutamic acid, sugar, and salts. They also ran a few samples on media such as peptones and beef extract. The titers on synthetic media have been too low for successful commercial use.

The Ben Venue Laboratories, one of the first commercial producers of bacitracin, used a medium of soybean meal and starch and obtained titers averaging 40 units per ml. with a range of 20 to 150 units per ml. The laboratory production in shake flasks differs somewhat from plant production in the composition of the medium for maximum titers. The rapid growth and high activ-

ity of the organisms when vigorously aerated in tank culture apparently cause rapid deamination of the proteins and consequent early rise in the pH.

The addition of carbohydrates delays the early rise in pH until the bacitracin titer has climbed satisfactorily (Figure 1). There is some acid production from carbohydrates which neutralizes amines as well as a certain amount of protein-sparing action of the carbohydrate. All carbohydrates are not equally suitable. Dextrose, for instance, is rapidly oxidized to acid and reduces the pH sharply to such low levels that growth is reduced; bacitracin titers are then very low. Calcium carbonate will buffer the medium to allow fairly good titers. Dextrose and sucrose under these conditions allow the production of fairly high titers, but maltose is extremely antagonistic to bacitracin production.

A production medium composed of soybean meal and a carbohydrate such as dextrose, sucrose, or starch has been reported (9) to give titers of more than 100 units per ml. in fermentation periods of 36 to 48 hours.

In shake-flask culture the organisms apparently do not as actively deaminate the amino acids of the proteins. Carbohydrates are not usually needed and in fact often result in lowered titers when added to soybean meal medium.

EARLY COMMERCIAL PRODUCTION

Ben Venue Laboratories started bacitracin investigations in 1945 in their plant at Bedford, Ohio; by 1946 they were producing appreciable quantities of the new antibiotic in the equipment formerly used for the surface culture production of penicillin.

Although the Ben Venue process was definitely a small scale venture utilizing glass bottles as fermentation vessels, sufficient bacitracin was produced to treat a variety of infections by topical administration and to evaluate the new substance as a chemotherapeutic agent.

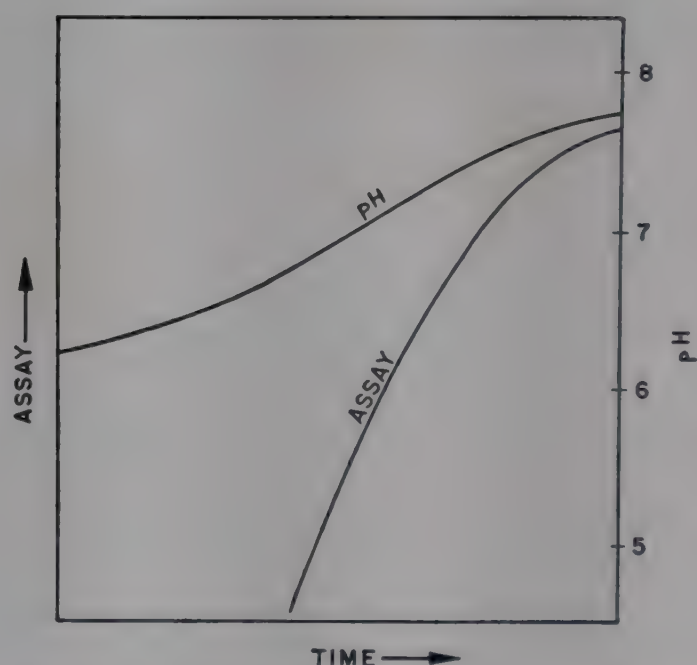


Figure 1. Assay and pH Characteristics in Normal Bacitracin Fermentation

Late in 1946, Commercial Solvents Corp. independently approached the problem of production of bacitracin by attempting the production under submerged conditions. The proved economics of submerged penicillin production made this type process seem the most attractive. The laboratory work showed that titers on submerged growth runs would be as high or higher than in similar media in static culture.

Therefore, in June 1947, Commercial Solvents completed a research and license agreement with Ben Venue and operated the bacitracin process for them until their own pilot plant for the submerged production was in operation near the end of that year.

Commercial Solvents, using existing fermentation facilities at the Terre Haute plant, produced bacitracin on a semicommercial scale until late in 1950 when its new antibiotic plant went on

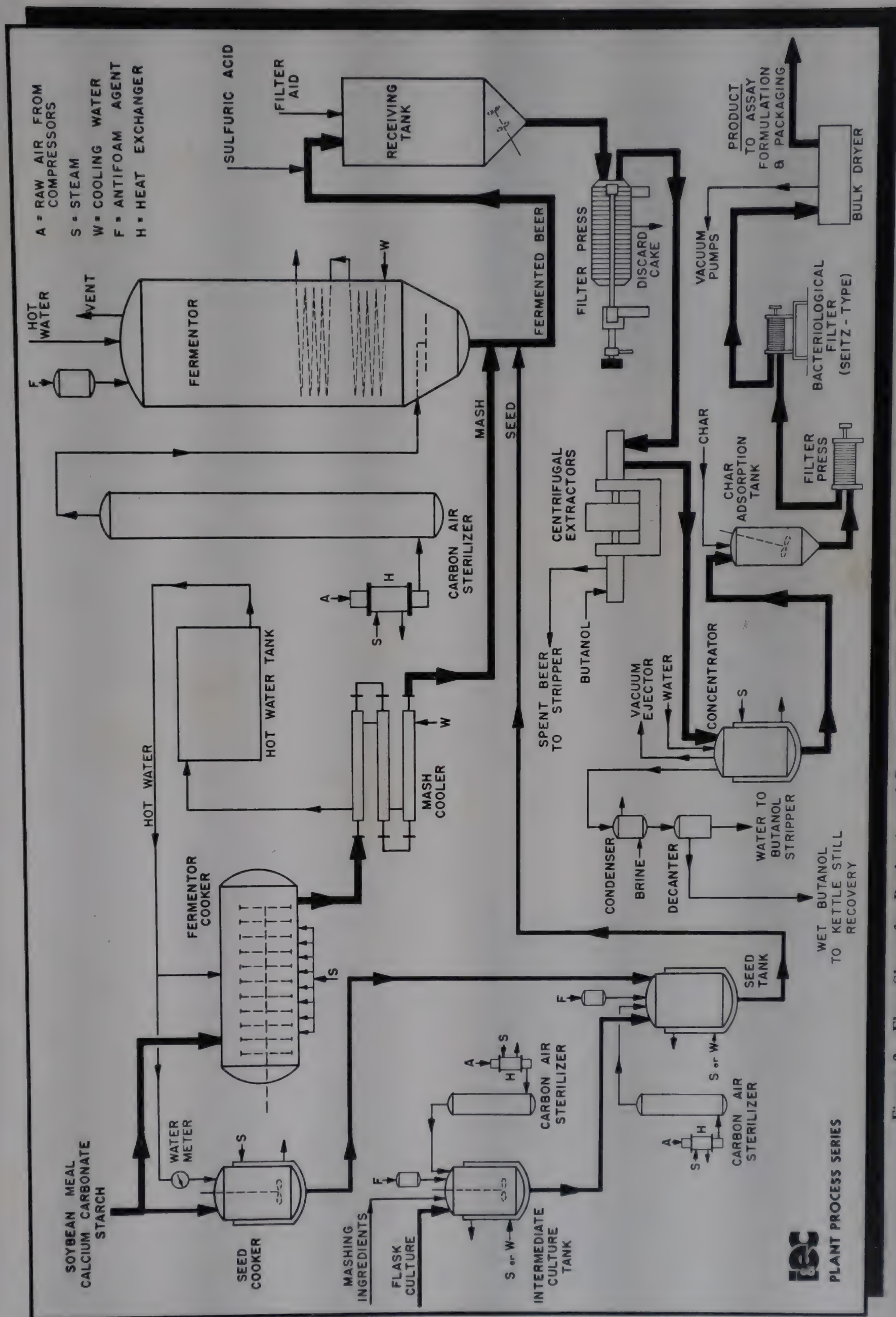
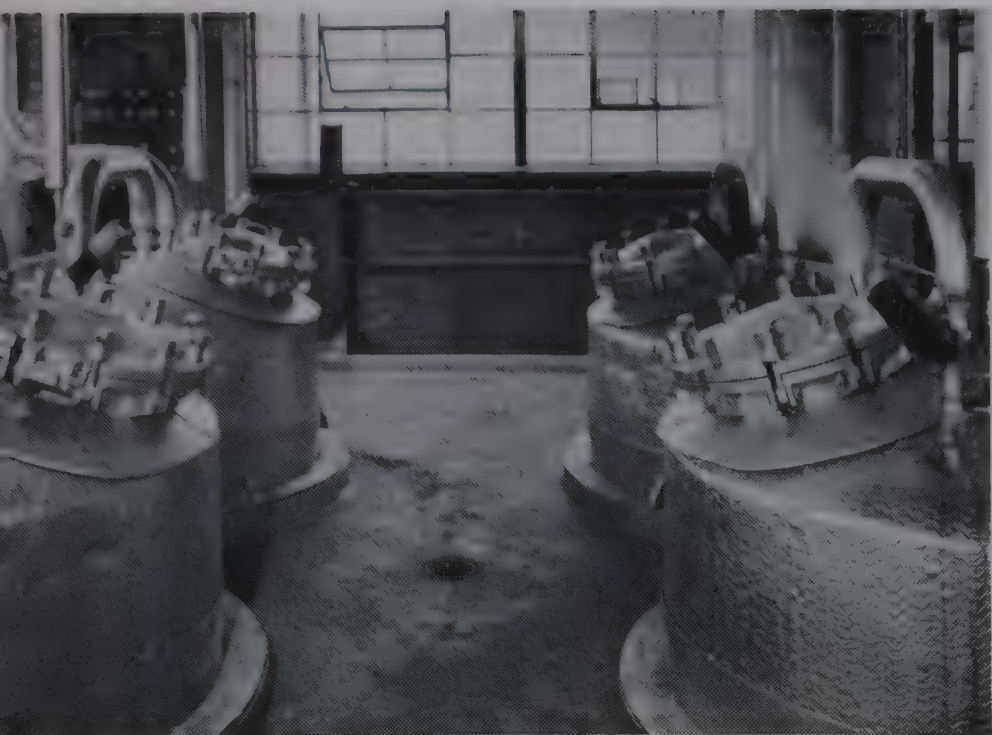


Figure 2. Flow Sheet for Production of Bacitracin at Terre Haute, Ind., Plant of Commercial Solvents Corp.

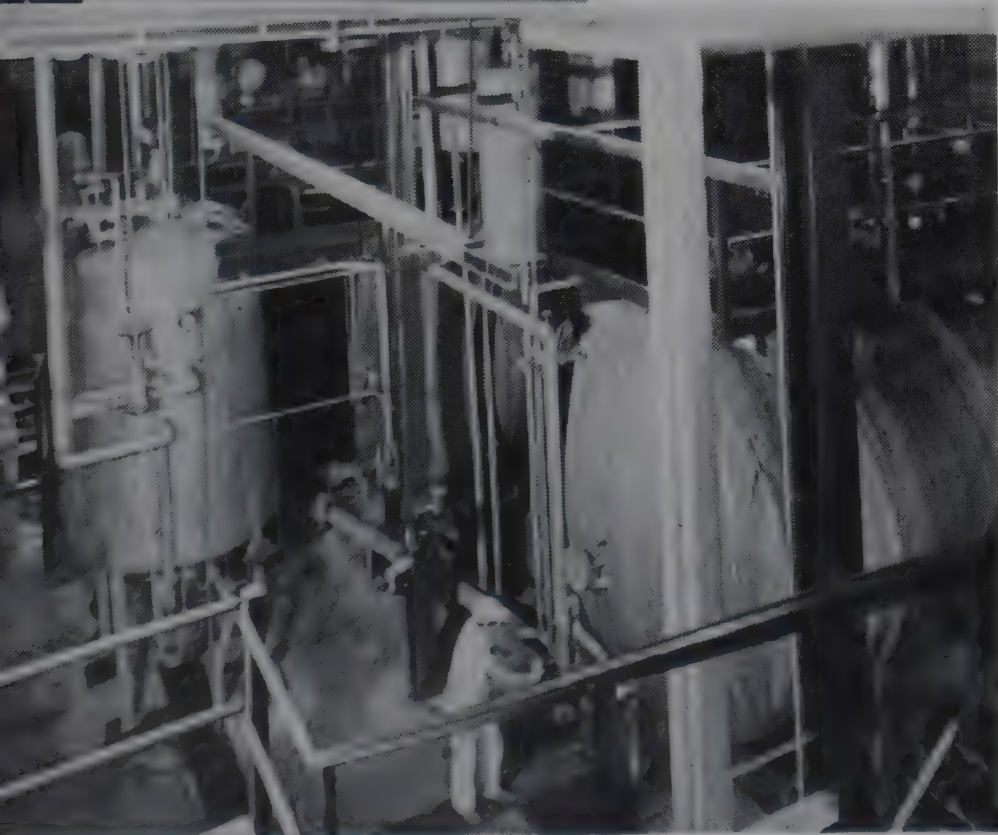


Seed tanks



Most of the fermentation operations are controlled from this central panel

Seed and fermentor cookers



stream. Commercial Solvents is the only major producer of bacitracin at the present time. The detailed description of the new plant which follows brings out the importance of the combination of microbiology, chemistry, and engineering—biochemical engineering—to the successful design and operation of a modern antibiotic plant.

COMMERCIAL SOLVENTS' TERRE HAUTE, IND., PLANT

A fundamental consideration in any industrial aerobic fermentation process is provision for an adequate supply of sterile compressed air. This presented no new problem for the Commercial Solvents organization since it had operated an aerobic penicillin process since early in 1944 (3). As a matter of fact, air for the new bacitracin plant is provided by the same central system which furnishes air for the adjacent penicillin plant. Even prior to construction of the penicillin plant, Commercial Solvents had put into operation another aerobic fermentation for the production of riboflavin.

Air System

Compressors are of the single-stage reciprocating type (4E) driven by synchronous motors (9E). Just prior to the completion of the new bacitracin plant, the capacity of the central unit was increased by the addition of a six-stage centrifugal compressor (5E) driven by steam turbine (24E). Capacity of the new compressor is 4000 cubic feet per minute with discharge pressure of 42 pounds per square inch gage.

Two reasons for the selection of this type compressor were: first, space considerations meant that any other type would require an addition to the existing building, and, secondly, the demand for the exhaust steam from the turbine made this type compressor economically desirable.

Air from the compressors passes through after-coolers of the shell-and-tube type. From the after-cooler the air goes through a trap from which condensed moisture and entrained oil are drained periodically.

One of the problems that faced the engineers designing the new plant was selection of an effective and economical method of air sterilization. Lee (9) has pointed out that numerous methods have been used successfully by the industry. These include: exposure to high temperature, ultraviolet light, or electronic precipitation; scrubbing with caustic, acids, or disinfectant solutions; and filtration through columns packed with cotton, slag wool or glass wool, or activated carbon. Columns packed with activated carbon were finally selected as the type equipment most desirable for air sterilization for the new bacitracin plant.

Experience had shown that it was essential that raw compressed air passing through carbon-packed towers had to be heated above the dew point in order to ensure a sterile air supply. For this reason, small steam heated preheaters of the tube-and-shell type were installed in the air line just before it entered the bottom of the carbon air sterilizers.

The temperature attained was not accountable for the difference in sterility of the air secured, as it was only in the range 40° to 60° C. It was assumed that, without heating, the carbon bed was eventually penetrated by air-borne droplets which formed as the air cooled below its dew point in expanding through the controlling inlet valve. These droplets evidently carried bacteria and bacterial spores from the surface of the carbon bed into the fermenting media.

Each intermediate culture tank, seed tank, and fermentor is provided with its own individual carbon air sterilizer and preheater. These are shown on the flow sheet (Figure 2). The air sterilizers are of varying sizes depending on the volume of air handled. The design is the same in each case, with air entering the bottom of the tower and passing through a bed of 8 to 14 mesh activated carbon (3E), then leaving the top of the tower sufficiently free of active bacteria to be used in the fermentation. A sketch

TABLE VII. VESSEL DATA

Item	Capacity, Gallons	Material of Construction ^a
Intermediate culture tank	150	Stainless steel ^b
Seed tank	1,200	Stainless steel ^b
Seed cooker	1,200	Carbon steel ^b
Fermentor cooker	12,000	Carbon steel ^b
Fermentor	24,000	Stainless steel ^b
Hot water collecting tank	24,000	Carbon steel
Beer receiving tank	24,000	Stainless steel
Vacuum concentrator	600	Glass-lined ^b
Char adsorption tank	200	Stainless steel

^a Stainless steel is Type 304.^b 1½-inch magnesia block insulation (8E).

of a carbon air sterilizer is shown in Figure 3. The carbon towers are sterilized with live steam each time the fermenting vessel (culture tank, seed tank, or fermentor) is sterilized. In other similar installations carbon towers have been used for several years without replacement of the beds. There appears to be little or no permanent deactivation resulting from use.

Culture Development and Fermentation

The general procedure for the microbiological production is to grow the culture of *Bacillus subtilis* (Tracy) on agar or to preserve it in the spore stage, dried on sterilized soil. A small quan-

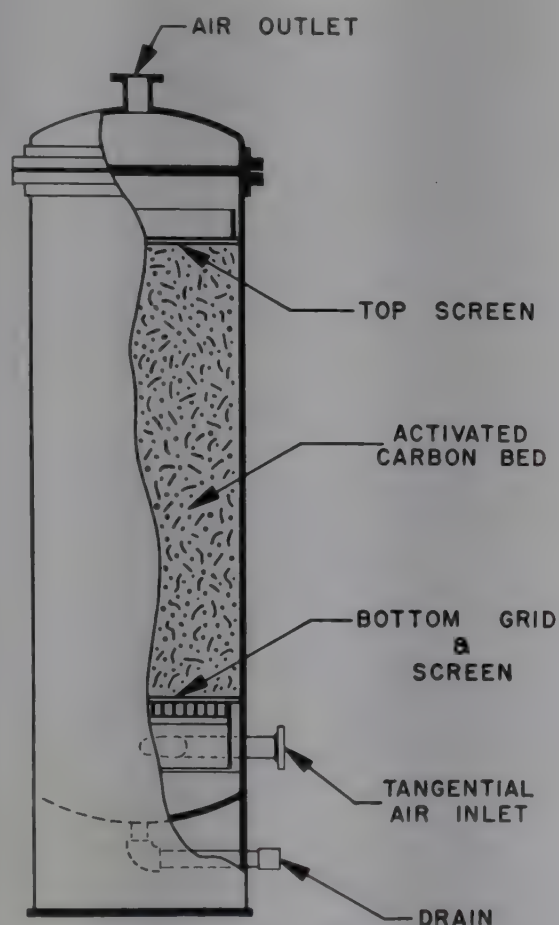


Figure 3. Cutaway Diagram of Carbon Air Sterilizers

tity of the soil is transferred aseptically to a 4-liter shake flask of peptone or tryptone broth. After the flask has been on the shaker for 18 to 24 hours at a controlled temperature of 37° C., the culture is ready for use in inoculating the intermediate culture tank in the plant.

The intermediate culture tank is made of stainless steel and has a capacity of 150 gallons. This tank along with other vessels in the plant is listed in Table VII. Mashing ingredients are sterilized by means of steam in the jacket while being agitated with a vertical mixer. After cooking, the mash is cooled by circulating water through the same jacket. The culture from the flask is introduced through a short rubber hose connection which has been previously sterilized by steam.

After inoculation, sterile air is passed through the culture tank for a period of approximately 6 hours; adequate growth has then taken place and the contents are blown by sterile air into a seed tank previously charged with cooked mash and cooled to 37° C.

The seed tank is similar in design to the intermediate culture tank, but has a capacity of 1200 gallons; it is also constructed of stainless steel and equipped with a jacket for either cooling or heating.

Sterile air is introduced into the seed tank until the growth cycle has reached the point of greatest reproductivity. The contents of the tank are then blown with sterile air into a fermentor which previously has been partially charged with cooked mash. The fermentor filling process is completed after inoculation.

The fermentors are vertical stainless steel vessels of welded construction, with a capacity of 24,000 gallons (Figure 4). Each

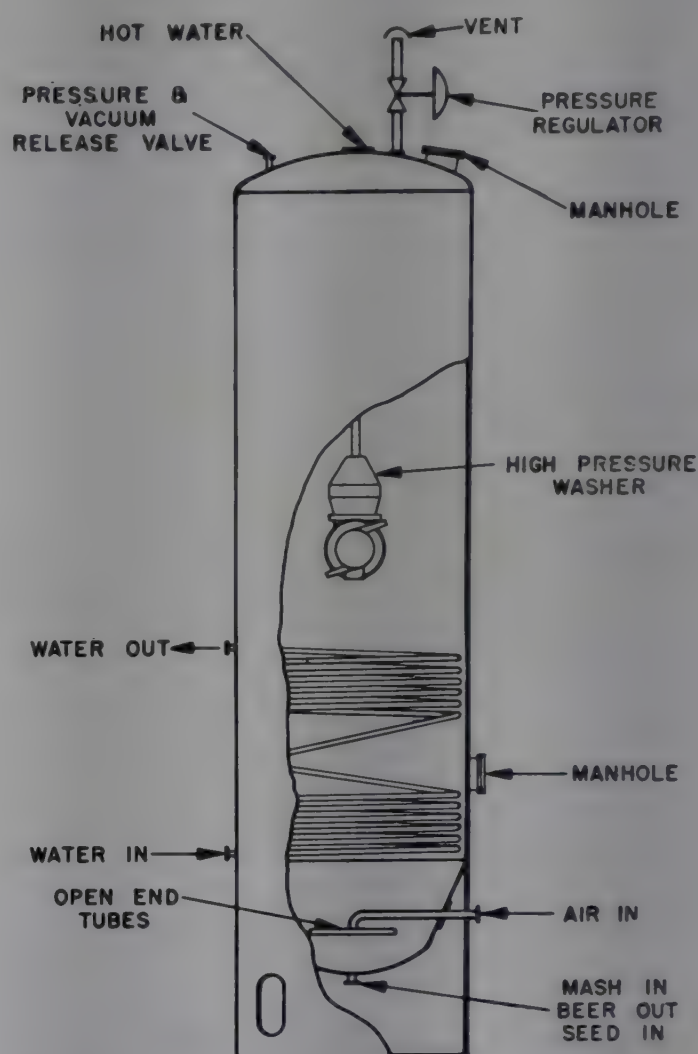


Figure 4. Cutaway Diagram of Bacitracin Fermentor

fermentor is provided with a conical bottom and the lower half of the fermentor is cooled by means of 2-inch outside diameter stainless steel tubing water coils. The temperature of the fermenting medium is controlled automatically by regulation of the water flow through the coils.

Sterile air is sparged through spiders of 1-inch open-end stainless steel pipes situated near the bottom of the fermentor. The air flow is measured by means of an orifice on the inlet side of the carbon filter and is regulated automatically by a control valve (11E) at this same location. The pressure of the fermentor is held at 5 pounds per square inch gage by means of a control valve (11E) on the vent line. The fermentors are located outside of the building and each is filled, inoculated, and emptied through the bottom valve.

As the fermentation progresses there is a very gradual rise in the pH and a more abrupt increase in the rate of production of bacitracin. This is shown by Figure 1. Since it is not possible to have an immediate assay of the bacitracin content, the optimum fermentation time has been determined from past experience.

Throughout the fermentation cycle, foaming occurs frequently

and is controlled by the addition of an antifoam agent previously sterilized by heat. The antifoam used is a 50:50 mixture of mineral oil and a synthetic antifoaming chemical.

Cooking

Two types of cookers are provided in the bacitracin plant: seed cookers of 1200-gallon capacity and the fermentor cookers of 12,000-gallon capacity.

The seed cooker is of carbon steel construction, jacketed in a fashion quite similar to the seed tanks. Water is added to the seed cooker through a batching meter (17E) which shuts off the flow when the correct volume is reached. Mashing ingredients consisting of soybean meal, calcium carbonate, and a small

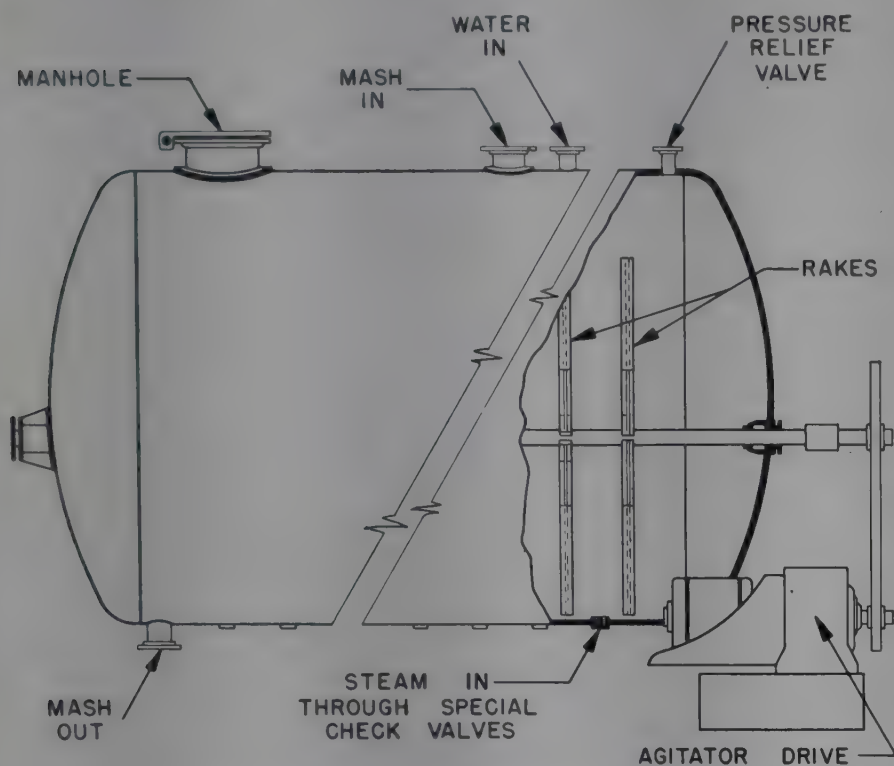


Figure 5. Details of Fermentor Cooker

amount of starch are added by means of a mechanical conveyor (12E). The charge volume of the seed cooker is 800 gallons. The mash is heated by means of steam in the jacket and agitated by a top-entering agitator. After cooking, the hot mash is blown to the seed tank by means of steam pressure. It is cooled to fermenting temperature in the seed tank, while being held under pressure by sterile air.

The fermentor cooker is shown in Figure 5; it is a horizontal carbon steel vessel equipped with a stainless steel rake type agitator. The cooker is charged with approximately 9000 gallons of water, measured in a liquid-level gage glass, and with dry ingredients from the mechanical conveyor (12E). The proportions of the mashing ingredients are approximately the same as for the seed cooker.

The mash is heated by sparging live steam through fifteen specially designed check valves (6E), equally spaced along the bottom of the cooker. The mash is heated to 100° C. with the vent valve open in order to displace the air. The vent valve is then closed, and the temperature is raised to 121° C. and held at that temperature for 60 minutes. During the entire period of cooking the agitator is run.

At the completion of the holding period the hot mash is pumped with a single-stage open-impeller centrifugal pump through a mash cooler to the fermentor. The mash cooler is a double pipe type with mash passing through the inside tubes and water through the annular space. The inside tubes are Type 304 stainless steel tubing and the jackets are carbon steel. Water leaving the jackets of the cooler is close to 65° C. This is collected in a 24,000-gallon hot water storage tank and used for charging subsequent fermentor or seed cookers and also for washing emptied fermentors.

Recovery

Recovery of the bacitracin from the fermented beer is shown diagrammatically by the flow sheet (Figure 2). At the completion of fermentation the beer is pumped to a 24,000-gallon, conical-bottomed stainless steel receiving tank. The pH of the fermented beer is lowered by introducing sulfuric acid into the stream after it leaves the fermentor. The acid is pumped by a piston type proportioning pump (15E) and is mixed with the beer by means of several sharp bends in the pipeline to the receiving tank.

After the fermentor has been emptied it is thoroughly washed by means of a rotating nozzle type washer (2E) originally developed for cleaning oil tankers. Water under 200 pounds pressure is pumped by means of a two-stage centrifugal pump from the hot water collecting tank to the cleaner. Approximately 180 gallons per minute are pumped to the washer. After a 12-minute hot water wash the fermentor is sterilized under 15 pounds steam pressure for a period of 6 to 12 hours.

The acidified beer in the receiving tank is agitated by means of a two-speed side-entering agitator (16E), installed as low as possible in the cone. The speed of the agitator is controlled by liquid-level instruments (1E) in the tank. As the liquid in the tank reaches the predetermined level, the agitator is started at slow speed. At a higher level in the tank the faster speed is automatically cut in to maintain better agitation of the larger volume. As the tank is emptied the procedure is reversed.

Filter aid (13E) is conveyed to the receiving tank from the warehouse by a mechanical conveyor (22E) and is added while the tank is being vigorously agitated. The normal concentration is 1 pound of filter aid for each 5 gallons of beer, but this may be raised or lowered depending on the nature of the beer.

The beer containing the filter aid is pumped through a 36-inch plate-and-frame filter press (21E) provided with aluminum plates and frames. The presses are equipped with motor-driven hydraulic opening and closing devices. The press cake containing filter aid and bacterial cells is discarded and the clear filtrate flows

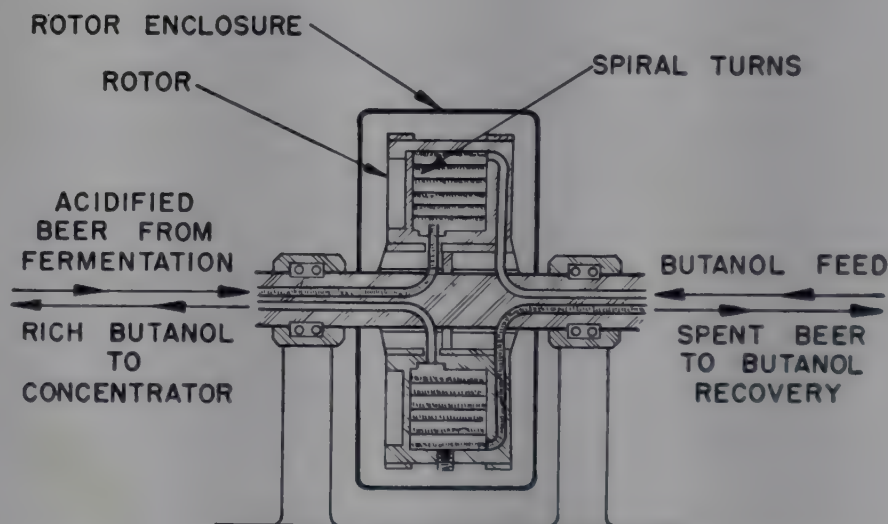


Figure 6. Schematic Cross-Sectional View of Rotor on Centrifugal Extractors

to a surge tank. To date, use of the press cake as a salable by-product has not been demonstrated. However, the growth in the bacitracin fermentation is quite similar to that in the penicillin process, and it is conceivable that feed supplements could be obtained from the press cake if suitable purification and drying procedures are worked out.

From the surge tank the filtered beer is pumped to a battery of countercurrent centrifugal solvent extractors (19E) where the bacitracin is extracted from the beer with butanol. The beer-to-butanol ratio is approximately 4 to 1; the beer feed rate to an individual extractor is 4.5 gallons per minute. The extractors are stainless steel and operate with a rotor speed of about 2000 r.p.m. The butanol and the beer pass countercurrently through a spiral

path provided in the extractor rotor. The intimate contact between the solvent and the aqueous layer brings about the extraction of the bacitracin from the beer by the butanol. A cross-sectional sketch of an extractor rotor, shown in Figure 6, indicates schematically the principle of operation; the spacing between the spiral layers is grossly exaggerated for the purpose of clarity.

An individual extractor is normally operated continuously for 8 hours and then taken off the line for a 1-hour wash with dilute phosphoric acid. Occasionally the extractors are washed with hot soda ash solution.

Butanol in the spent beer discharged from the extractors is recovered in a conventional distillation system using a perforated-plate still column as a stripper with subsequent redistillation in a kettle still, provided with a bubble-cap column and decanter. The solubility of the solvent is approximately 9 gallons of butanol per 100 gallons of beer; sizable amounts of butanol are recovered in this manner.

Butanol containing the bacitracin from the extractors is collected in a holding tank and then charged to a 600-gallon glass-lined concentrator (18E), equipped with a three-stage vacuum ejector (10E). A constant boiling mixture of butanol and water is evaporated at a pressure of 40 mm. of mercury and temperature of 28° C., the vapors being condensed in a brine-cooled closed condenser. The distillate passes to a decanter with the butanol-water taken off to the stripper and the wet butanol collected for charging to the kettle still.

The operation of the concentrator is semicontinuous in that butanol is charged intermittently along with small amounts of water until the entire volume of butanol from one fermentor (about 4000 gallons) has been processed. At this point there remains in the concentrator an aqueous concentrate of approximately 100 to 150 gallons.

The aqueous concentrate is char-treated (7E) at an acid pH for 30 minutes in an agitated 200-gallon stainless steel tank. This char treatment removes colors and odors from the concentrate. The normal amount of char is 0.5 pound per gallon of concentrate. The char slurry is filtered through a 12-inch plate-and-frame filter press, the plates and frames of which have been specially coated (14E) to prevent pickup of iron.

The filtrate then passes through a Seitz bacteriological filter (20E) to remove any bacteria which may have developed during the processing.

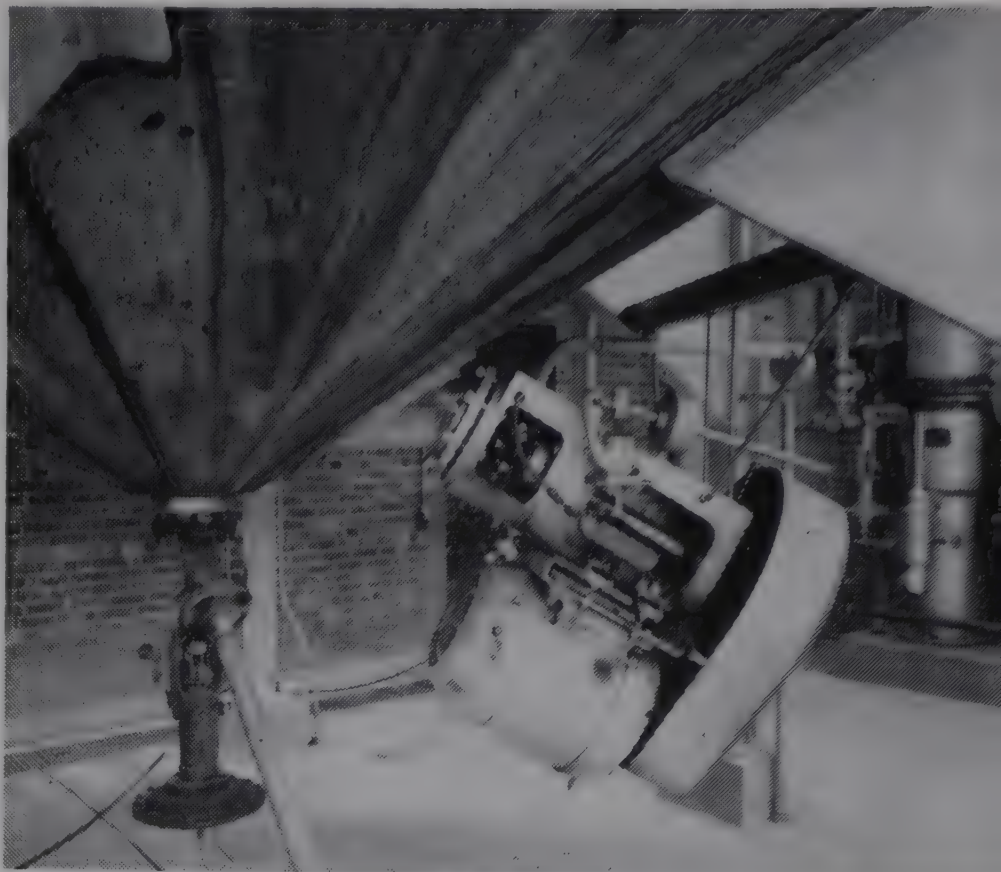
The bacteria-free concentrate then goes to a bulk tray dryer operating at a pressure of 100 to 200 microns and temperature of 65° to 75° C. After the water is removed, the remaining nearly white powder is ready for pharmaceutical formulation.

START-UP OF NEW PLANT

An elaborate system of automatic controls has been designed for the plant. When completely installed, the system should provide remote and coordinated actuation of almost every important valve in the fermentation unit. For example, it will be possible to set up all the valves involved in the inoculation of a fermentor by merely selecting one position of a multiport pilot valve located on a panel board and tied into the pneumatic actuation system. An installation of this type should prove of special value in fermentations because the possibility of contamination resulting from wrong valve settings should be eliminated. Final installation of the automatic controls has been delayed because of minor technical difficulties and shortages of essential items of equipment.

A demand for the facilities, which were being temporarily used for the production of bacitracin, required starting operations in the new plant before many of the automatic valves and even some of the auxiliary equipment had been installed. For instance, for several months, the cookers were charged without the aid of the conveyors by carrying and dumping the raw materials manually.

One of the tenets of any microbiological process is cleanliness.

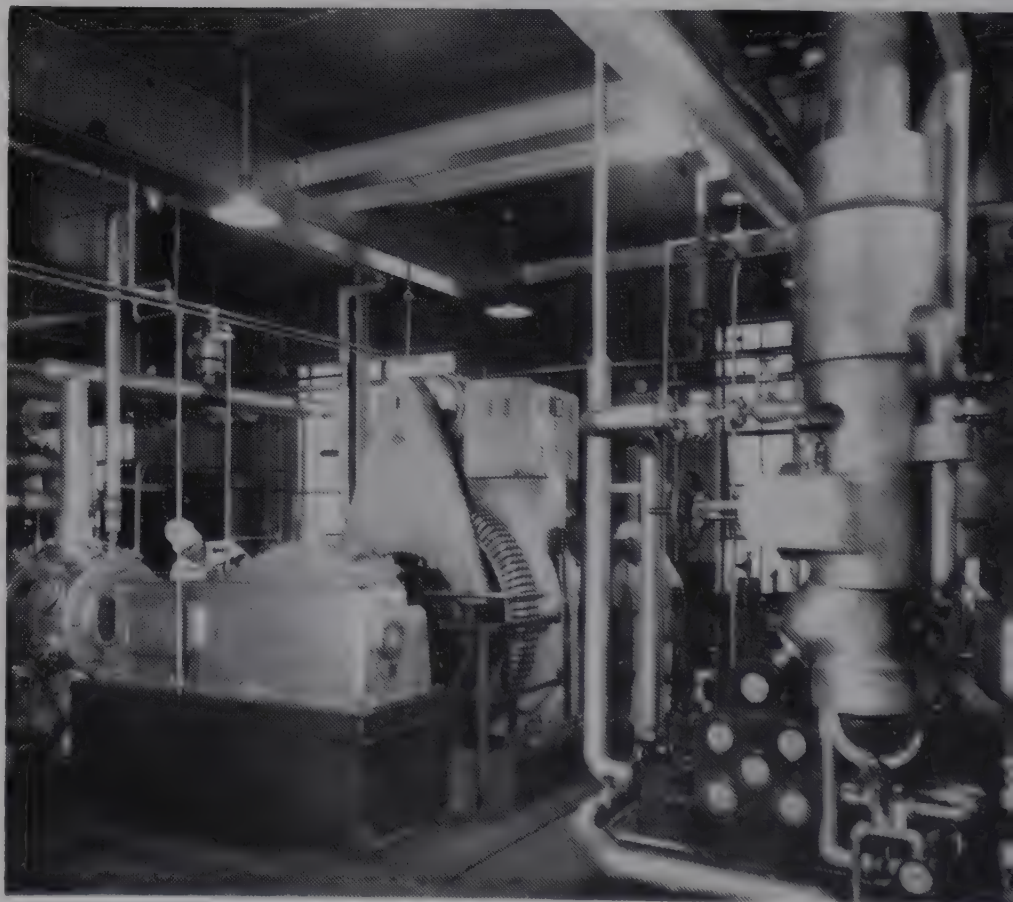


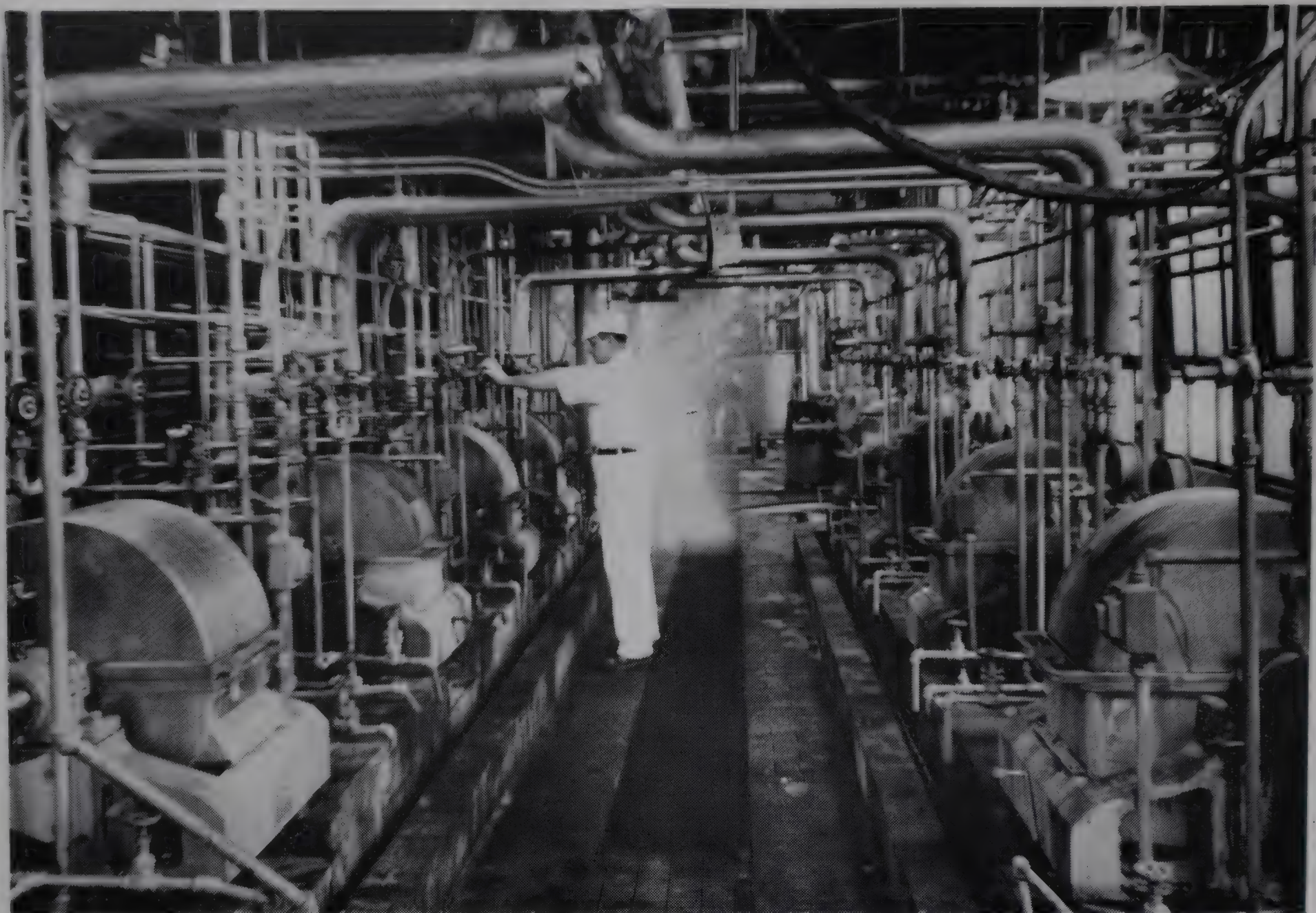
Filter-Aid mix tank with side-entering agitator

Return-bend heat exchanger on roof is used to cool cooked mash



Compressors provide air for fermentation





Centrifugal Countercurrent Solvent Extractors Recover Bacitracin from Fermented Beer

Therefore, actual operations were preceded by a thorough physical cleaning of tanks, pipelines, and other equipment. Hot caustic and hot soda ash washes were run in all tanks and through all lines. The fermentor cookers, seed cookers, seed tanks, and fermentors were entered and inspected for foreign matter and good drainage. Line valves and the mash pump were disassembled and inspected. The entire system was sterilized with steam under a pressure of 15 pounds per square inch. The surface temperature of bleeder lines to traps and of line and valve parts was determined by checking with special thermosensitive wax pencils (23E) to ensure that sterilizing temperatures were being attained throughout.

After the cleanup and sterilization, there followed a period of several weeks of exploratory operation. During this period the efficiency of the special fermentor washers (2E) was studied. The principle of one of these washers is illustrated in its most simplified form by an ordinary lawn sprinkler. The washing interval was established by determining the time elapsing between two successive sweeps of a wash stream across the center of an opened top manhead of a fermentor. The time for this complete rotational cycle was found to be approximately 12 minutes.

Inspection of the emptied fermentors after a 12-minute wash revealed that an excellent job had been done. There were no indications of mash holdup any place in the fermentor. Apparently the splash from the high water velocity obtained was sufficient to cleanse even the shadow areas behind and around the cooling coils.

Control

With the plant in full scale commercial operation, the chemical, physical, and bacteriological control in the bacitracin fermenta-

tion is extremely important, even though not particularly unique. The temperatures of each fermentor, seed tank, and cooker are indicated on a circular chart temperature recorder-controller; pressures are similarly recorded.

Samples of the fermentation vessel contents are periodically withdrawn aseptically to test for titer, contamination by foreign bacteria, pH, and occasionally other special determinations. The normal sampling interval is 12 hours. However, for special runs or during periods of suspected contaminations more frequent sampling is the rule.

Samples are always taken on vessel contents before any inoculum is added in order to determine if true sterility actually existed. These samples usually give ex post facto indications; by the time a small amount of sample is subcultured, streaked on an agar substrate, and allowed sufficient time for development, the fermentation in the seed tank or even in the fermentor is well on its way to completion. However, the record provided by these samples is essential to trace the source of any contamination that might develop.

Unlike a chemical process, microbiological work permits no "degree" of purity; sterility is an absolute condition. Whereas the chemical process is probably never run without foreign molecules among its reactants, the microbiological process frequently cannot be run if there is so much as a single foreign cell living. Such a cell or spore can in a matter of hours result in astronomical numbers of similar cells which "take over" the fermentation.

Contamination in bacitracin fermentation is particularly serious for it can stop further production of the antibiotic and

often can destroy that amount which has already been produced.

Laboratory

The new bacitracin plant includes a well equipped media and control laboratory, two incubator rooms, and a transfer room. The incubator rooms are provided with shakers oscillating at 100 cycles per minute and a stroke of $1\frac{1}{4}$ inches; the temperature can be controlled to $\pm 1^\circ$ C. within the range 24° to 40° C. By having the two incubator rooms it is possible to maintain separate cultures at two different temperatures.

The transfer room is lined with a dull-finish plastic for cleanliness and to reduce the amount of glare from the numerous ultraviolet lights. The room is frequently washed with disinfectant solutions and is thoroughly sprayed just prior to use to settle any dust particles.

One technician works 8 hours per day, 5 days per week preparing media, washing, sterilizing, and pouring agar plates, and sterilizing sample flasks. Culture transfers are made each day by a graduate bacteriologist. Fermentation samples are accumulated overnight and are assayed during the day. Provision is made for the necessary assays over week ends and holidays by arrangements with the penicillin plant laboratory.

ECONOMICS

An approximate distribution of the current production costs of bacitracin in the Terre Haute plant is shown in Table VIII. Operating supplies include filter aid and butanol; these two are the major items of cost.

TABLE VIII. PRODUCTION COST BREAKDOWN

	Per Cent
Raw materials	25
Operating labor	8
Operating supplies	40
Depreciation, insurance, taxes	10
Utilities	6
Miscellaneous	11

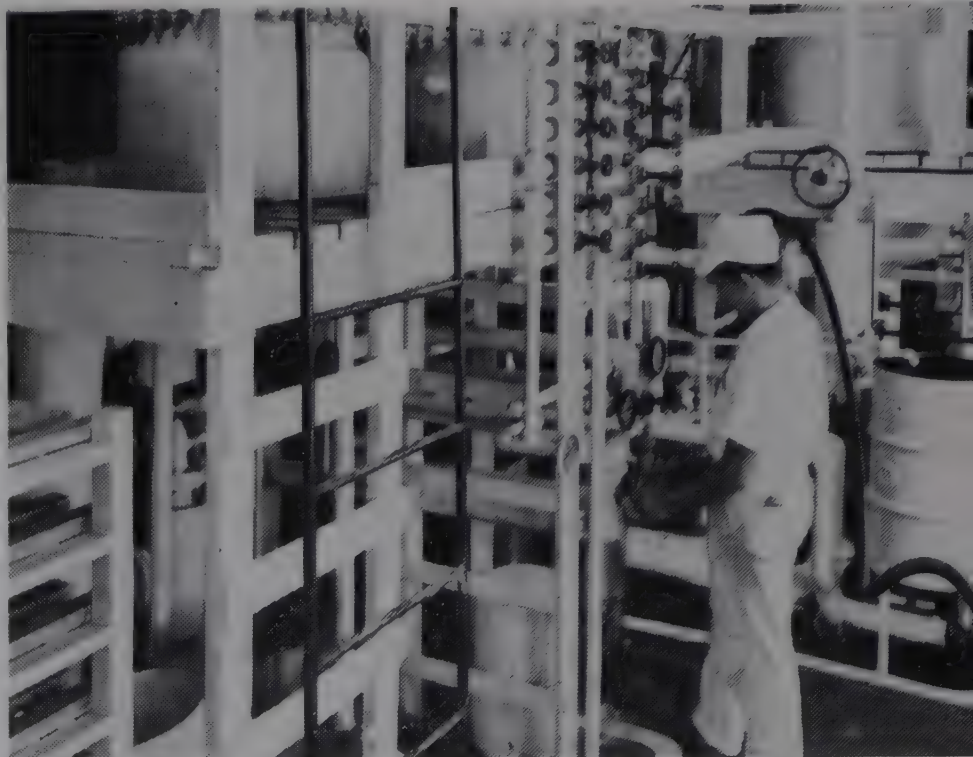
The location of the bacitracin plant adjacent to the penicillin plant and the similarity of the processes has made it possible to use the existing supervisory personnel for operation of both plants. A process foreman and a technical supervisor oversee the operations of each shift. Each foreman, at the present time, has had over 20 years' experience in fermentation and chemical production work. The technical supervisors are considerably younger, but each has an engineering or scientific degree.

There is a great demand for low pressure (15 to 20 pounds) steam for sterilizing processing equipment and for mash cooking. The exhaust steam from the turbine driving the new centrifugal air compressor boosted the quantity of steam available at this pressure. Water conservation measures are important to the process economics, and they have been given special consideration. The hot water discharged from the mash cooler is collected and re-used to charge the cookers and wash the fermentors. Water from the cooling coils in the fermentors is used to wash down the discarded cake from the filter presses.

Future

It is difficult, if not impossible, to predict with any accuracy the future of a new chemotherapeutic agent. Bacitracin, just as any other chemical of commerce, will survive only if it can remain in a competitive position both from the standpoint of cost and of utility. To maintain this competitive position, present research is directed in three general fields—fermentation, recovery, and application investigation.

The fermentation research involves investigation of many possible media with the idea of increasing the bacitracin produced in a given volume or using lower cost raw materials for the

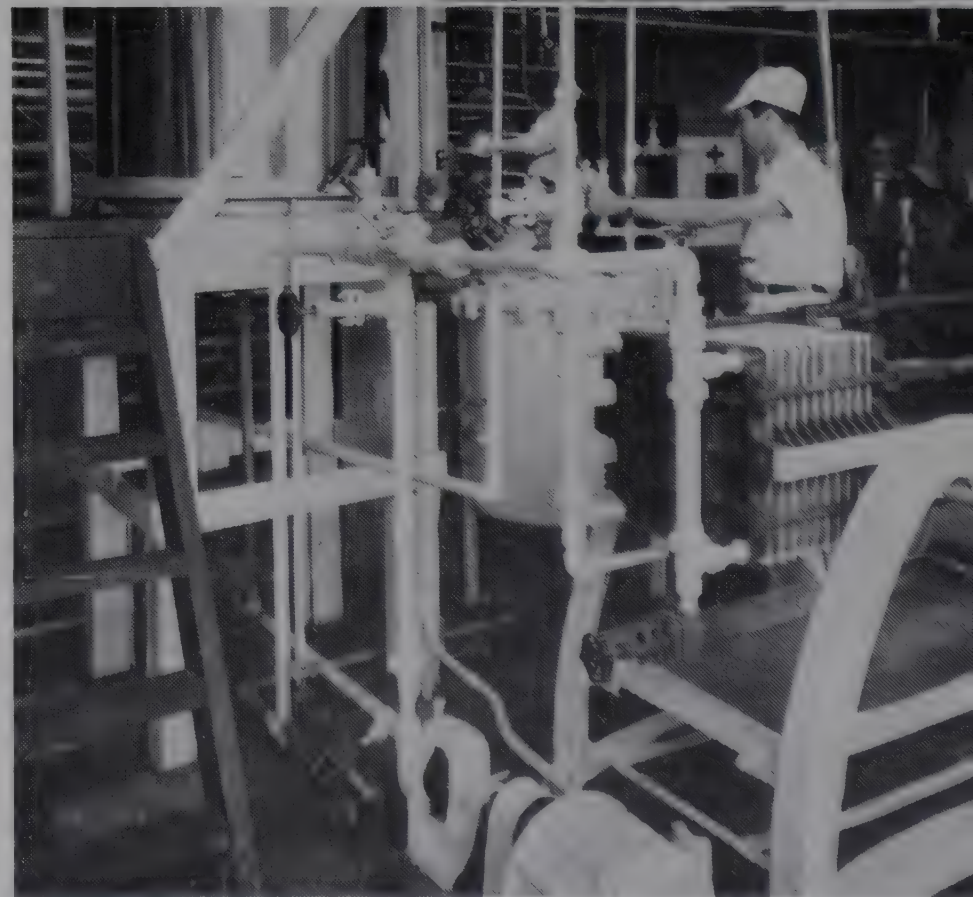


Butanol removal in glass-lined vacuum concentrators



Seitz bacteriological filter

Char adsorption and filtration



same production of bacitracin. The use of various chemical additives is continually being investigated. The tremendous increase in the production of penicillin was mainly due to improvements in the fermentation technique.

The recovery of the bacitracin from the fermented broth, being a multistep process, offers much opportunity for improvement in over-all yield. It is also hoped to obtain a product of higher purity through improvements in recovery methods.

Only through prolonged clinical tests of bacitracin will data necessary for the physician be accumulated, and a definite antibiotic spectrum be established.



Fermentor Area during Construction

Small tower (left) is carbon air sterilizer

The new bacitracin plant in Terre Haute has been designed with versatility as a keynote. The fermentation section could quite readily be converted for the production of most any other aerobic fermentation product. The recovery section is not quite so versatile, but without much difficulty could be adapted to other processes: penicillin, for instance, could be recovered in the bacitracin equipment by making only minor changes.

One of the newer aspects of antibiotic production is the use of these products as animal growth-promoting factors. Preliminary tests have shown that bacitracin has outstanding possibilities in this field and Commercial Solvents is already producing bacitracin in 50,000-gallon fermentation vessels in Peoria, Ill., for this purpose.

Production of bacitracin for feeding purposes is quite similar to the fermentation for pharmaceutical uses. However, the recovery is much less complicated and involves only evaporation, drying, and blending operations.

The bacitracin feed supplement, which is being produced in carload lots in the Peoria plant, is said to stimulate growth and reduce the mortality of poultry and swine. The large size of the bacitracin molecule is believed to prevent significant absorption from the intestinal tract at the levels used in the feeds. The fact that it is not readily destroyed by enzymes of the intestinal tract offers an additional advantage.

The commercial product contains 5 grams of bacitracin per pound of supplement. For most finished feeds the recommended level is 2 pounds of the supplement per ton of feed.

The development of this type of feed supplement is one of the many indications that the antibiotic industry is far from static. Increased knowledge and application of the principles of biochemical engineering mean that improved production and recovery methods as well as more universal use of the antibiotics can be expected in the coming years.

ACKNOWLEDGMENT

The authors wish to express their appreciation for the valuable assistance of Sylvan B. Lee, director of microbiological research and development, Commercial Solvents Corp., in the preparation of this article.

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- (14) Scudi, J. V., Coret, I. A., and Antopol, W., *Ibid.*, **66**, 558 (1947).

Processing Equipment

- (1E) Automatic Control Co., St. Paul, Minn., Prob-o-trol.
- (2E) Butterworth System, Inc., Bayonne, N. J., Type C washing machine.
- (3E) Carbide and Carbon Chemicals Corp., New York, N. Y., Columbian carbon Grade G.
- (4E) Chicago Pneumatic Tool Co., New York, N. Y., air compressors.
- (5E) Clark Bros. Co., Inc., Div. of Dresser Industries, Olean, N. Y., centrifugal and axial flow compressors.
- (6E) Commercial Solvents Corp., Engineering Div., Terre Haute, Ind., specially designed check valve.
- (7E) Darco Corp., New York, N. Y., activated carbon G-60.
- (8E) Eagle-Picher Lead Co., Cincinnati, O., insulating material Type DE 85.
- (9E) Electric Machinery Mfg. Co., Minneapolis, Minn., synchronous motors.
- (10E) Elliott Co., Jeannette, Pa., vacuum ejectors.
- (11E) Fisher Governor Co., Marshalltown, Iowa, flow and pressure regulators.
- (12E) Hapman-Dutton, Inc., Saginaw, Mich., Cat. No. 5000, meal conveyor.
- (13E) Johns-Manville Corp., New York, N. Y., Super-Cel filter aid.
- (14E) Lithgow Corp., Chicago, Ill., Lithcote coating.
- (15E) Milton-Roy Pump Co., Philadelphia, Pa., proportioning pump model MDI-58-74 spec. type.
- (16E) Mixing Equipment Co., Rochester, N. Y., *Bull. B-76*, beer receiving tank agitator.
- (17E) Neptune Meter Co., New York, N. Y., liquid batching meter.
- (18E) Pfauter Co., Rochester, N. Y., glass-lined equipment.
- (19E) Podbielniak, Inc., Chicago, Ill., centrifugal extractor Model 6080.
- (20E) Republic Filters, Inc., Paterson, N. J., stainless steel filter Model 200/16.
- (21E) Sperry, D. R. & Co., Batavia, Ill., Cat. No. 6, plate-and-frame filter presses, Type E.H.C.-L.
- (22E) Stephen-Adamson Mfg. Co., Aurora, Ill., Cat. No. 140, filter-aid conveyor.
- (23E) Tempil Corp., New York, N. Y., Tempilstiks, specified melting point wax pencils.
- (24E) Worthington Pump & Machinery Corp., Moore Turbine Div., Wellsville, N. Y., *Bull. 1961*, compressor drive turbine.

Reagent Grade Chemicals



Eimer & Amend Laboratory Where Small Quantities of Specialty Products Are Prepared

R. L. DEMMERLE
Associate Editor

in collaboration with

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THE quality of reagent chemicals ranks with the precision of scientific instruments as a major physical determinant of the accuracy of the work of chemists and chemical engineers. Almost every development in chemistry and its allied fields may be attributed, directly or indirectly, to improvements in the manufacture, performance, and standardization of laboratory apparatus and chemicals—the tools of the chemist.

The modern scientist, although quick to lavish praise and attention on improved instrumentation, has at the same time taken for granted the predictable nature and high quality of the chemical reagents that line his laboratory shelves. Behind their informative labels and constantly increasing variety, however, lie years of effort by many individuals and organizations.

The quest for purity began in the era of the alchemist. Most recipes for the much sought philosopher's stone contained detailed instructions regarding the purification of the ingredients (12, 13, 18). Failures in transmutation of the base metals were often ascribed to the existence of impurities in the starting materials (17).

Many of the operations now used for the purification of chemicals had their origin during this period. Because of the religious fervor of the times, the recorded descriptions and nomenclature of these operations had a strong spiritual flavor—that is, distillation was termed ascension and condensation, descension. The important purifying step now known as sublimation was likened by the alchemists to an "upward flight of doves" and called ex-

altation or elevation. When the operation was repeated several times, it was supposed to yield the quintessence of the original substance (19).

The dawn of the science of chemistry placed new emphasis on the need for experimental materials of a reasonably certain composition. Although the early chemists were able to secure some of their materials from apothecary shops, much of their time had to be spent in the preparation of their reagents from natural substances. Many of the basic discoveries during chemistry's first 100 years were coincident with the synthesis or fractionation of laboratory reagents from crude commercial materials (14). It was common practice for the chemists of that time to exchange with their colleagues the purified compounds they had prepared, in order to gain a greater variety of reagents in their laboratories.

About the middle of the nineteenth century, the demands of photography and increased medical and pharmaceutical knowledge led to the beginning of a fine chemicals industry in Europe, principally in Germany (5). The chemist benefited immeasurably from this development and until World War I reagents from German firms such as C. A. F. Kahlbaum and E. Merck filled a high percentage of the demands of the world's laboratories.

In America, the industrial revolution brought the establishment of some of our currently well-known fine chemical concerns, but there was a much greater emphasis on the building of a heavy chemicals industry. Laboratory supply houses were forced to import the majority of their reagents already packaged for distribution or in bulk for subsequent packaging. To a lesser extent, they shopped among the domestic chemical industries for selected cuts of its production suitable for reagent use.

American enterprise in reagent manufacture began to take form about the beginning of this century. Merck & Company, an established importer, began domestic manufacturing about this time (9). Baker and Adamson was founded in 1901 and a few years later the firm was bought and enlarged by the General Chemical Company (6). In 1904, J. T. Baker, one of the founders of Baker and Adamson, formed his own firm at Phillipsburg, N. J. (6). Other American companies began to devote more of their attention to the manufacture of reagent grade chemicals, but the infant industry still had to face the keen and experienced competition of foreign firms in the American market. As recently as 1914, the majority of fine chemical and reagent firms in business in this country were either the branch offices or sales agents of German companies (4).

The British blockade of Germany in World War I caused the United States to expend more effort in developing its limited facilities for the production of fine chemicals. The reagent segment of the industry acquired its share of attention but the shortage of laboratory grade chemicals, especially organics, grew worse and had assumed critical proportions at the time the United States entered the war. The appearance of reagents of inferior quality on the market caused President Stieglitz of the AMERICAN CHEMICAL SOCIETY to appoint a special committee on analyzed reagents under W. F. Hillebrand to recommend specifications for these materials (10). A year later this committee was succeeded by a permanent committee under the chairmanship of E. Emmett Reid (6).

The wartime shortages caused chemists once again to prepare many of their reagents. In 1914, C. J. Derick of the University of Illinois initiated a system of vacation-time laboratory work during which students prepared the reagents most urgently needed for the coming semester. In 1916, Roger Adams took over the project and enlarged it to supply chemists outside the university (6). At about this same time the Imperial College at South Kensington in England founded an exchange bureau through which British chemists and institutions could barter chemicals (20).

In the decade that followed the war, American facilities for the manufacture of laboratory reagents expanded considerably.

Eastman Kodak organized its organic chemicals department in 1919 as a domestic source of fine organic reagents. The Mallinckrodt Chemical Works announced the creation of a reagent chemical department in 1922, a consequence of its long experience in the production of photographic and other fine chemicals (6). Four years later the General Chemical Company built a plant at Marcus Hook, Pa., to expand the capacity of its Baker and Adamson division (8). In 1927, Merck & Company consolidated with Powers, Weightman, and Rosengarten Company, another fine chemicals company (9). Although there was a tendency on the part of some to return to German sources, American firms by the mid-twenties were in a position to supply a wide variety of reagent grade chemicals.

Improvement in the techniques used in manufacturing reagent grade chemicals has resulted in raising their general level of purity. Absolute purity, as determined by sensitive analytical procedures, has been approached in many products. Its complete achievement, however, would be technically and economically infeasible and cannot be considered the goal of the industry. Instead, the working principle that is followed in the preparation of a reagent is to lower and keep its impurities beneath the concentrations that would interfere with the course of the preponderant majority of the reactions in which it may be used. In those cases where a commercially available reagent is not sufficiently pure for a particular purpose, the user or manufacturer, working on special order, can usually carry the purification to the desired higher state.

STANDARDIZATION

As the reagent industry grew, it became apparent that the increased exactness of chemistry made it necessary that the chemist be informed and assured of the maximum limits of impurities in his reagents. Critics asserted that the term "chemically pure" was by itself meaningless (15) and that the initials C.P. stood only for the conscience of the producer. Similar fault was found with the indiscriminate use by British manufacturers of the term "analytical reagent"; one authority claimed that the initials A.R. merely designated a product that was all right (20).

It is generally believed that informative labeling of reagents began in Germany in 1888 when Krauch, under the auspices of E. Merck, published the first book on standards and methods of testing reagent chemicals (11). Labels began to appear with the analyses for impurities given in the ambiguous terminology of trace, faint trace, and very faint trace, a marked contrast to current labels which often list the results of as many as fourteen different determinations. According to Haynes, Eimer & Amend of New York was the first firm to market a line of reagents bearing an exact analysis of the impurities present (7).

Early attempts in this country to establish uniform standards for drugs, medicines, and some chemicals were the publication of the first Pharmacopeia of the United States in 1820 (16), and the first National Formulary in 1888 (3). Subsequent revisions of these works have included numerous specifications for chemicals suitable for reagent use. However, the emphasis placed on medicinal and pharmaceutical chemicals has limited their value to chemists. In recognition of this situation the AMERICAN CHEMICAL SOCIETY's Committee on Analytical Reagents in 1921 published a series of specifications and testing methods for common laboratory reagents. Since that time, this work has been republished and enlarged until it now includes specifications for more than 150 reagents (1, 2). These standards serve as a valuable yardstick in maintaining the high and uniform quality of the reagent grade chemicals made in this country.

EDGEWATER, N. J., PLANT OF EIMER & AMEND

Eimer & Amend, a major supplier of laboratory apparatus and chemicals, began in 1851 as a drug store on the lower East Side

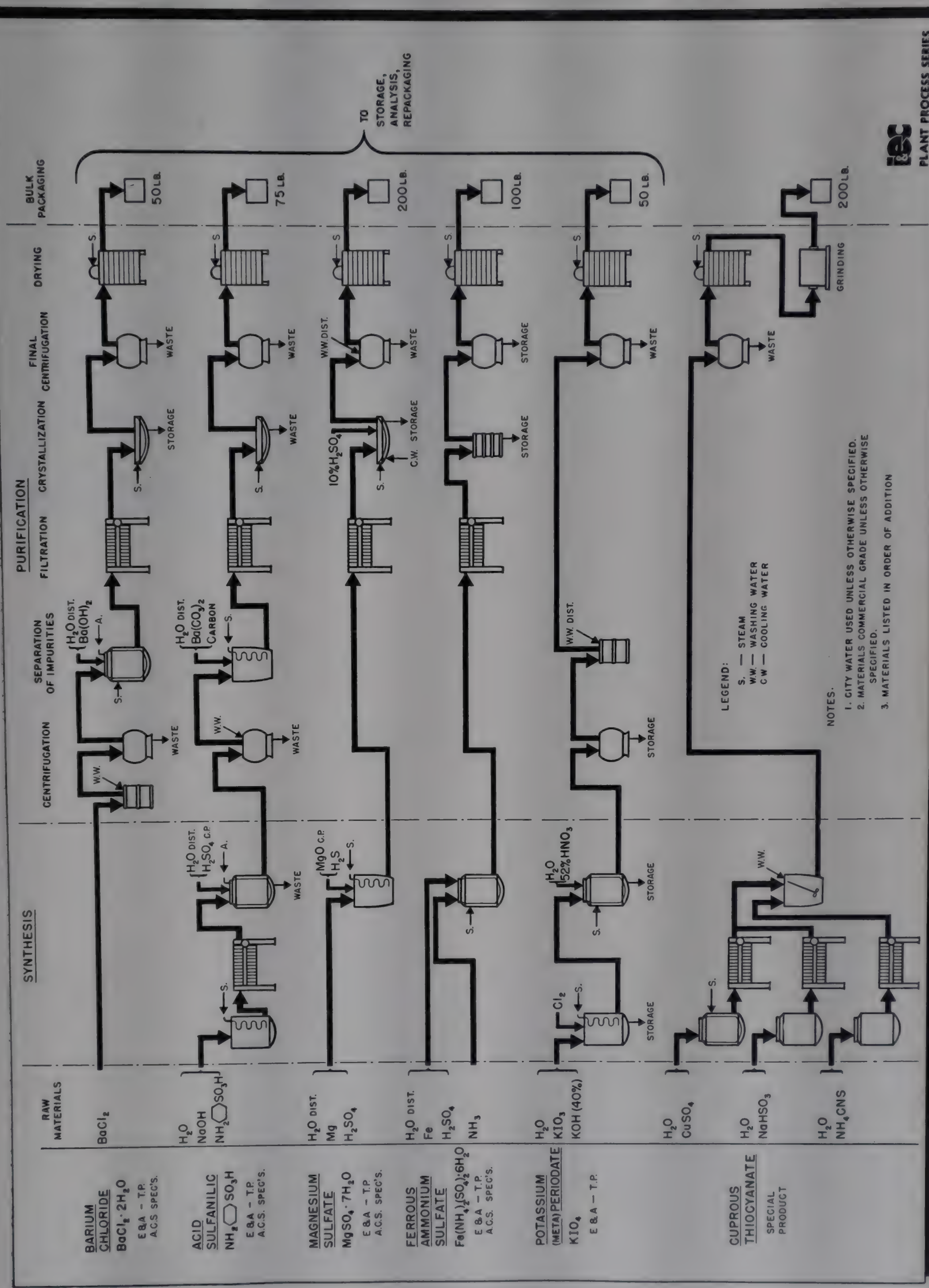


Figure 1. Flow Sheets for Synthesis and Purification of Six Reagent Grade Chemicals Processed at the Edgewater, N. J., Plant of Eimer & Amend

of New York City. The company's interest in the handling of reagent grade chemicals was a direct outgrowth of its early activities in the purification of drugs and the compounding of pharmaceutical preparations. To meet the demands of laboratories in this country Eimer & Amend imported European-made apparatus and reagents, repackaging many of the latter under its own label after analysis. In addition to analytical laboratories, the company also maintained manufacturing laboratories for the preparation of biological stains, specialty products, and small quantities of reagents not obtainable from foreign or domestic sources.

World War I interrupted the flow of reagent chemicals to Eimer & Amend from abroad. To make up this deficiency the company undertook a brief manufacturing venture in a small plant in Newark, N. J., but wartime production operations were suspended in 1918, and the former practice of analyzing and repackaging reagents was resumed. This time, however, domestic sources provided most of the bulk reagents.

Eimer & Amend moved to new and more modern quarters in New York in 1940 after a major portion of its capital stock was acquired by the Fisher Scientific Company of Pittsburgh, Pa. The manufacturing laboratories of the chemical products department were enlarged to produce a greater variety of special reagents of the less common type such as silver lactate, calcium permanganate, barium bromate, and chromous acetate. These materials are made in small batches to supply a limited but steady demand.

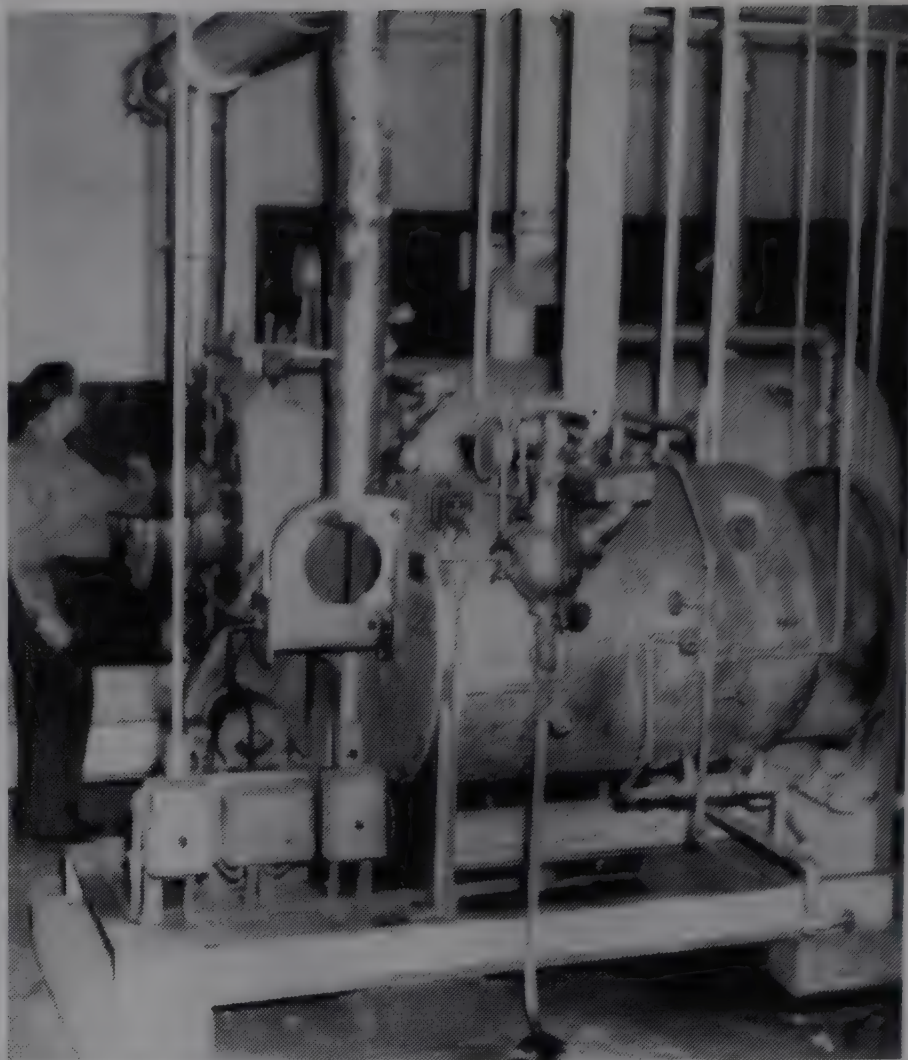
In the summer of 1944, the capacity of the chemical products department was further expanded by the acquisition of plant facilities in Edgewater, N. J., for the production of some of the major staples in Eimer & Amend's line of Tested-Purity reagents and Tissuemat, a paraffin-base mounting material. The poundage and variety of reagents manufactured at the plant have grown steadily since operations began in the fall of 1944. At present about 100,000 pounds of eighty reagent grade chemicals are produced annually which, after final analysis and packaging in the New York plant of the company, constitute about 20% of the Tested-Purity reagents handled by Eimer & Amend, the Fisher Scientific Company, and their branches and outlets in the United States and Canada.

The Edgewater plant is located about 100 yards inland from the west shore of the Hudson River at a point opposite uptown New York City, and trucking time from the main quarters of the company in lower Manhattan is within 1 hour. It is situated on a 1.25-acre rectangular site and consists of three one-story, flat-roofed brick buildings. Each contains 5000 square feet of floor area and is sprinkler equipped.

The main building houses the plant offices, the control laboratory, and facilities for the manufacture and packaging of Tissuemat. The other two buildings are devoted to the production of reagents and are about 10 yards distant from the main building. These two share a common wall and fire-door passageway; one contains the production units and steam plant and the other is reserved for the storage of raw materials, empty bulk containers, and finished products. The latter structure also has a mechanically ventilated vault for flammable materials; it is equipped with a fire door, raised doorsill, and a spark-resistant floor. The main building and the storage building have outdoor loading platforms of small truck tailboard height.

Electrical power in the form of 220-volt, 3-phase, 60-cycle current is supplied the various production units by a bus duct that runs the length of the production building. The steam plant, which is located in a 24 × 24 foot room in the rear of this building, contains an oil-fired, 15-hp., high pressure boiler for process steam and an oil-fired, 30-hp. low pressure boiler for low temperature steam, the preparation of distilled water, and space heating. Commercial utility gas (535 B.t.u. per cubic foot) is distributed to the units that require it by a 4-inch service line.

Process Water. About 65% of the process water require-



Boiler Room, Edgewater Plant

High pressure boiler, foreground; low pressure boiler, rear

ments of the plant are met by single-distilled water, 25% by deionized water, and 10% by municipal water. The choice of whether to use raw or treated water depends on the step in which it will be employed, the nature of the operation, and the specifications being sought in the finished product. The municipal water, as supplied, is of a good quality, containing a maximum of 15 p.p.m. total hardness.

Analysis of Municipal Water, %

Sulfate	0.001
Chloride	0.001
Iron	0.0001

Its composition permits usage in many of the processes during the preliminary steps wherever concentration is not effected. In the preparation of iron compounds, for instance, the iron content would be of little consequence.

The distilled water is made by condensing, continuously or as required, a portion of the low pressure steam in a water-cooled block tin condenser located near the ceiling of the boiler room. The condenser feeds a 500-gallon horizontally mounted aluminum storage tank which is situated on a mezzanine in the same room. The water can be prepared at a top rate of 32 gallons per hour at a cost of 3 cents a gallon. It is delivered by gravity flow through three 0.75-inch Saran pipes to the vicinities of the process units in which it is used. Local delivery is accomplished by flexible hose connections to these lines.

During the summer months deionized water is used as a replacement for distilled water; its price of 4 cents a gallon is offset by the economy resulting from the decreased operation of the low pressure boiler. It is prepared by passing raw municipal water through a 20-gallon-per-hour ion exchanger which is located on the mezzanine of the boiler room. Water leaving the exchanger is stored in the distilled water tank from which it is distributed through the Saran lines. An automatic conductivity measuring device, set for a minimum resistance of 50,000 ohms, notifies when the deionizer's charge should be replaced. At vari-

ous other times during the production year, deionized rather than distilled water is used in preparations requiring a process water of this type. All waste process water in the plant is disposed of through the municipal sewage system. Because of the low ionic concentration of the waste no harmful complications arise from this procedure.

Operations. Batch processes, handling from 300 to 1000 pounds of material at a time, are used exclusively in the plant. Because of this, the equipment units are modest in size and are selected on the basis of their versatility of operation and ease of cleaning. The general rule followed in the purchase of a new item of equipment is that it must be usable in the preparation of at least five different reagents.

In method of operation the Edgewater plant resembles more closely a flexible manufacturing pilot plant than it does a static production-type installation. As many as ten different reagents may be in various stages of processing at one time, each preparation taking from 7 to 10 days for completion. Fluctuating market demands for reagents make it unlikely that any given day's schedule will repeat itself in exact detail. A material may be made three times in 1 year and not at all during the next. For this reason, a rigid engineering approach to operational planning or process design is infeasible.

Production schedules are formulated with the purpose of making maximum use of the plant's equipment at all times. The recurrent preparations of the more common reagents form the basis of the schedules and the production of the slower selling materials is worked into this framework. A proposal to manufacture a reagent not previously made at the plant is evaluated in light of the following:

1. General immediate need
2. Possibility of overstocking
3. Potential role in research, development, and analytical work
4. Extent of complementation in existing products and facilities of reagents already produced
5. Industrial hazards incident to its manufacture
6. Amount of additional equipment needed
7. Cost, availability, and purity of starting materials

Preparations. The great majority of the reagents prepared at the plant are solid materials. With the exception of distillation, the plant is equipped with units capable of carrying on most of the classic operations: filtration, evaporation, crystallization, and drying are used in almost every preparation.

The various plant units are either of special design or of a standard type modified to gain greater flexibility of operation. Many are made of stainless steel or chemical stoneware, and others are rubber- or glass-lined; they provide a variety of surfaces from which the most appropriate for a given set of reactants may be chosen.

The batch type of processing employed and the constantly changing nature of the production schedule make it necessary to operate the equipment as isolated units much of the time. This situation also offers hand loading and unloading as the most flexible manner of moving solid materials from one unit to another. The transfer of process solutions between equipment units, either directly or through a filter press, is accomplished by means of a centrally located, rubber-lined pump equipped with 1.25-inch hose connections of varying lengths (3E).

The plant's three evaporating pans and four of its seven reaction kettles are situated under a mechanically ventilated Transite hood in one corner of the production area. All reactions involving the evolution of significant quantities of gases or vapors are conducted in this portion of the plant.

Reagent grade chemicals are prepared by three general types of processes:

1. Purification of the commercial grade compound
2. Synthesis from high purity starting materials
3. Synthesis from commercial grade starting materials with subsequent purification

The following preparations (Figure 1) are described to demonstrate the wide variety of reactions and operations used to manufacture standardized, high quality reagent chemicals. With the exception of cuprous thiocyanate, a special product, and potassium metaperiodate, these chemicals meet A.C.S. specifications of purity.

BARIUM CHLORIDE

The preparation of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), Eimer & Amend's Tested-Purity reagent (according to A.C.S. specifications), consists of the purification of a commercial grade of the material by the removal of about 96% of its calcium chloride and strontium chloride impurities. These compounds interfere with many of the quantitative reactions in which barium chloride is employed.

	Analyses	
	Raw Material, %	Reagent Product, %
Insoluble	0.12	0.005
Alkali salts	0.45	0.05
Heavy metals (Fe)	0.005	0.0005
Strontium and calcium chlorides	1.08	0.035

The commercial material is received in 100-pound paper bags in a moist condition due to the hygroscopic nature of the strontium chloride and calcium chloride impurities. The major part of these alkaline earth chlorides is present on the surface of the barium chloride crystals and is removed by a primary washing and centrifuging operation.

A 1-ton working batch of the commercial material is divided into ten aliquots which are placed in open-top, rubber-lined steel containers of 15-gallon capacity and made into a slurry by the addition of 2 gallons of city water, at room temperature, to each container. Agitation is by a hand-manipulated, rubber-coated, steel paddle.

The containers are placed on a wooden platform at the level of the top of the centrifuge by a portable lift truck (9E) and are tilted manually to discharge their contents into the 26-inch rubber-lined basket of the centrifuge (5E). Each aliquot is centrifuged for 5 minutes, and the liquor is discharged to waste. This washing operation removes approximately 90% of the total strontium and calcium chlorides present. Only about 2.75% of the barium chloride is lost because its solubility is considerably less than the impurities under the conditions of the operation.

A secondary and final purification is effected by a recrystallization of the barium chloride from a saturated solution. The damp crystals from the washing operation are removed with type 304 stainless steel hand scoops from the centrifuge basket and weighed out in 300-pound quantities on a portable platform scale (2E). The saturated solution is formed by consecutively dissolving these batches in 60-gallon portions of distilled water in a 75-gallon steam-jacketed kettle (11E). To facilitate solution, the kettle is heated to 80° C. and the contents are agitated by air delivered through a glass nozzle.

Iron impurities are precipitated by adjusting the pH of the solution to 9, ± 0.5 , by the addition of approximately 0.25 pound of barium hydroxide of a technical grade to a batch of solution. The contaminants introduced by this latter material are negligible.

Physical removal of the precipitated iron impurities is effected by filtration of the solution through a neoprene-coated 12-inch eight-chambered filter press (4E, 8E). The filtrate is discharged into two glass-lined, steam-jacketed, steel evaporating pans, each of 60-gallon capacity (12E). A centrally located rubber-lined pump equipped with flexible connections is used for the filtration operation and the delivery of the solution to the evaporators which are located under a 30 \times 20 foot Transite hood in one corner of the main production area. The hood is serviced by a 1500-cubic-foot-per-minute fan.

The barium chloride solution is evaporated to about 20% of its original volume, and the residual liquor is ladled off by hand and



← Drying

↑ Crystallizing

Processing Reagent Grade Chemicals at
Edgewater Plant of Eimer & Amend

Reaction
Kettle ↓

↓ Centrifuging



led for future plant use as a technical grade product. About 1/2 of the original barium chloride raw material is lost, for immediate reagent purposes, in this recrystallization operation. In figures, when added to that lost in the primary washing step, presents a loss of 20% and a net reagent yield of about 80%.



Raw Materials Storage Room, Edgewater Plant

Magnesium ingots for preparation of reagent grade magnesium sulfate being weighed

The purified crystals are removed by hand from the evaporating pans, centrifuged, and dried in a steam heated, mechanical convection, tray dryer at 40° C. (13E). The dryer contains 18 trays (1.5 X 29 X 21 inches). Drying requires about 18 hours after which the material is scooped out of the trays and loaded into 50-pound, paper-lined, fiber drums for shipment to the packaging facilities for final analysis, packaging, and labeling.

SULFANILIC ACID

The preparation of sulfanilic acid, Eimer & Amend's Tested-Purity reagent (according to A.C.S. specifications), is also a purification of a technical product. In this case, however, it is first necessary to change the compound to the sodium salt to facilitate removal of the 1.2% (Fe₂O₃) iron impurity. After this step is completed the material is reconverted to its acidic form for further purification in which the other major impurity, 0.2% sulfate, is removed.

A 300-pound batch of the crude product is weighed directly from its original containers into a Type 304 stainless steel, coated, 75-gallon kettle (11E) containing a solution of 65 pounds of technical grade sodium hydroxide in 40 gallons of city water. The solution is heated to 80° C. and filtered, while still hot enough to prevent crystallization, through the filter press to remove the precipitated mixed iron hydroxides. The filtrate is discharged into a 60-gallon glass-lined steel kettle (11E), containing a solution of 84 pounds of sulfuric acid in an equal volume of distilled water. Reagent grade acid is used to prevent the addition of iron to the reactants. Air agitation, by means of a glass nozzle and hose connection to an air line, is employed to prevent local excesses of acid that might alter the course of the reaction or local excesses of base that might attack the glass surface of the kettle.

The slurry of precipitated sulfanilic acid is allowed to cool to room temperature and the excess liquor is drained to waste. The solid material is removed manually with Type 304 stainless steel shovels; it is placed in 12-gallon rubber drums and transferred to the centrifuge for washing. A 1-minute spray of city water at 20° C. is used for this purpose because of the inability of the material to pick up significant amounts of iron in this operation. The wash water, like the waste liquor, is discarded because of its high sodium sulfate content.

The wet sulfanilic acid is weighed and transferred to a 240-gallon stainless steel kettle (7E) heated by a Type 304 stainless steel steam coil. For every 100 pounds of sulfanilic acid, 100 gallons of distilled water, 10 pounds of barium carbonate of technical grade, and 1 pound of decolorizing carbon are added to the kettle. The entire charge is heated to 80° C. Barium carbonate is used for the precipitation of excess sulfate and the decolorizing carbon serves to remove various chromophoric compounds that were present in the original commercial product.

The material is cycled through the filter press to three glass-lined evaporating pans under the ventilating hood where it is evaporated to one fourth of its volume. After cooling it is removed from the pans by hand, centrifuged, and dried in the tray dryer at 50° C. (13E). The reagent is obtained in 70 to 75% over-all yield. It is shipped in 75-pound vinylite-lined drums to the packaging facilities. Its final analysis shows less than 0.02% ignition residue, and a sulfate content of less than 0.01%.

MAGNESIUM SULFATE

The preparation of magnesium sulfate (MgSO₄·7H₂O), Eimer & Amend's Tested-Purity reagent (according to A.C.S. specifications), consists of forming the salt by a single displacement-type reaction between metallic magnesium and sulfuric acid, precipitating heavy metal impurities from the resulting solution by treatment with hydrogen sulfide, and final purification by filtration and crystallization.

Magnesium oxide could be employed in the reaction more cheaply than metallic magnesium but most of the magnesite available contains over 1% calcium impurity which is difficult to separate from magnesium salts without the addition of further impurities. Any such separation would necessarily have to be performed in dilute solutions which would entail an uneconomical increase in the cost of concentrating the process solution preparatory to crystallization.

The metallic magnesium, used as received from the Dow Chemical Company in the form of ingots, contains less than 0.01% calcium and less than 0.005% iron, with insignificant quantities of other impurities. A portable platform scale is used to weigh out 60 pounds (three ingots) of the metal which are placed in a 110-gallon coil-heated stainless steel kettle (7E) to which 55 gallons of distilled water have previously been added. The kettle is located in the portion of the plant serviced by the hood-and-flower system.

The reaction proceeds by the slow addition of 200 pounds of commercial grade sulfuric acid, 66° Bé., to the kettle by means of a glass siphon. The rate of addition is kept low (approximately 40 pounds per day for a 5-day period), to prevent local accumulations of hydrogen under the hood. The main portion of the acid (185 to 190 pounds) is added by completely discharging the known weight contents of a carboy that is elevated by a mobile lift truck to a platform at the level of the kettle. Additional acid, as required to make up the 200-pound quantity, is weighed out in a glass container and added directly. Commercial grade acid may be used in spite of its iron content because this reaction precedes the iron removal step. The over-all formation of magnesium sulfate heptahydrate proceeds as follows:



As the reaction nears completion the temperature is raised to the neighborhood of 105° to 110° C. and is maintained at that

level until the pH of the solution is brought into the range of 4 to 5. Sufficient reagent grade magnesium oxide (about 2 pounds) is added to raise the pH to a level just over 9 and mercaptan-free hydrogen sulfide is bubbled through the hot solution for 5 minutes at a rate of approximately an ounce a minute. The gas is delivered to the solution by means of a glass tube at the end of a length of rubber tubing coming from the hydrogen sulfide cylinder. Control samples are removed from the kettle during the course of the gasification, filtered, analyzed for iron content, and their pH measured. Additional magnesium oxide is added if the pH is below 9.

The precipitated heavy metal sulfides (about 99% FeS) are removed by passage of the process solution through a filter press (4E). The filtrate is led into a glass-lined, jacketed, steel evaporating pan (12E). Sufficient reagent grade sulfuric acid, previously prepared in 10% solution with distilled water, is added to the filtrate to bring the pH down to 6. At this acidity the excess hydrogen sulfide is readily liberated on concentration of the solution. The small amount evolved (approximately 2 to 3 ounces) is collected by the hood over the open pan and vented to the atmosphere through the blower.

Concentration is continued at a temperature of 110° C. until a specific gravity of 1.38 (determined optimum for crystallization) is obtained. At this point, rapid cooling to 48° C. is effected by the introduction of city water at 20° C. for a period of 20 minutes into the jacket of the evaporating pan. Rapidity of cooling is essential to prevent the formation of crystals of the lower hydrates which occurs at temperatures in excess of 48° C. The desired heptahydrate is formed by crystallizing in the range 20° to 48° C.

The crystals of magnesium sulfate heptahydrate are removed from the evaporator with hand scoops, placed in 13-gallon rubber-lined steel containers and carried by hand truck to the rubber-lined centrifuge (5E) for washing with a spray of distilled water. The material is removed from the centrifuge and dried in the tray dryer for 18 hours at 40° C. (13E). The magnesium sulfate heptahydrate is obtained in 85% yield; it is packed in 200-pound quantities in vinylite-lined fiber drums for transfer to the analytical and packaging operations.

Specifications (1) for Magnesium Sulfate—Eimer & Amend Tested-Purity Reagent

	%		%
Insoluble matter	0.005	Calcium (Ca)	0.02
Acidity (as H ₂ SO ₄)	0.015	Heavy metals (Pb)	0.0005
Chloride (Cl)	0.0005	Iron (Fe)	0.0005
Nitrate (NO ₃)	0.002	Manganese (Mn)	0.0005
Ammonia (NH ₃)	0.002	Sodium (Na ₂ SO ₄)	0.02
Arsenic (As)	0.0002		

FERROUS AMMONIUM SULFATE

The preparation of ferrous ammonium sulfate [Fe(NH₄)₂(SO₄)₂·6H₂O], Eimer & Amend's Tested-Purity reagent (according to A.C.S. specifications), is another instance in which it is necessary to use the elemental form of the metallic ingredient to ensure a minimum of impurities in the final reagent grade product. The raw materials used in its preparation are scrap Swedish steel which contains 0.005% manganese and practically no other metallic impurities; sulfuric acid, 66° Bé., whose chief impurity is iron (0.2% FeSO₄) and of little consequence in the preparation of an iron compound; and commercial grade anhydrous ammonia. Because of the evolution of hydrogen and the use of ammonia in this process, it is carried out in the portion of the production area serviced by the hood-and-blower system.

A quantity of 85 pounds of steel scrap is degreased in Type 304 stainless steel containers (9-gallon capacity) by washing in carbon tetrachloride. After air-drying, the steel is added to 75 gallons of distilled water in a glass-lined, jacketed, steel kettle of 100-gallon capacity (11E). Acid addition is accomplished by elevating two carboys of acid (185 pounds each) consecutively to the level of the kettle's edge by a mobile lift truck and emptying

them by means of a glass siphon equipped with a stopcock. The second carboy is placed on a platform scale, which is elevated with it, in order to weigh out the exact amount of acid from the second carboy needed to make up the total acid requirement of 320 pounds for the reaction. The mixture is heated to 70° C. and held at that temperature until all of the steel is dissolved; this takes about 2 days. To the resulting ferrous sulfate solution, 56 pounds of ammonia are added by means of a glass tube nozzle and rubber tubing connection from an ammonia cylinder standing on a portable platform scale.

The ferrous ammonium sulfate solution is filtered through the rubber-lined filter press and the filtrate received in four rubber crystallizing drums (13-gallon capacity each). The solution is allowed to crystallize for 48 hours after which the crystals are separated from the mother liquor by centrifuging in the rubber-lined centrifuge (5E). The mother liquor is used in the composition of a subsequent batch where it is introduced after the metal-acid reaction. The ferrous ammonium sulfate, obtained in 85% over-all yield, is dried in the tray dryer (13E) for 18 hours and packed in 100-pound quantities in vinylite-lined fiber drums.

Specifications (1) for Ferrous Ammonium Sulfate—Eimer & Amend Tested-Purity Reagent

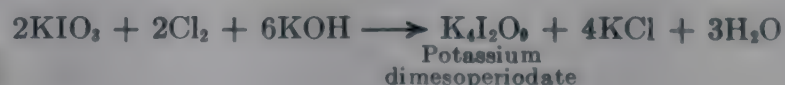
	%		%
Insoluble matter	0.010	Manganese (Mn)	0.015
Chloride (Cl)	0.003	Zinc (Zn)	0.003
Copper (Cu)	0.003	Not pptd. by NH ₄ OH	0.050
Iron (Fe)	0.010		

POTASSIUM METAPERIODATE

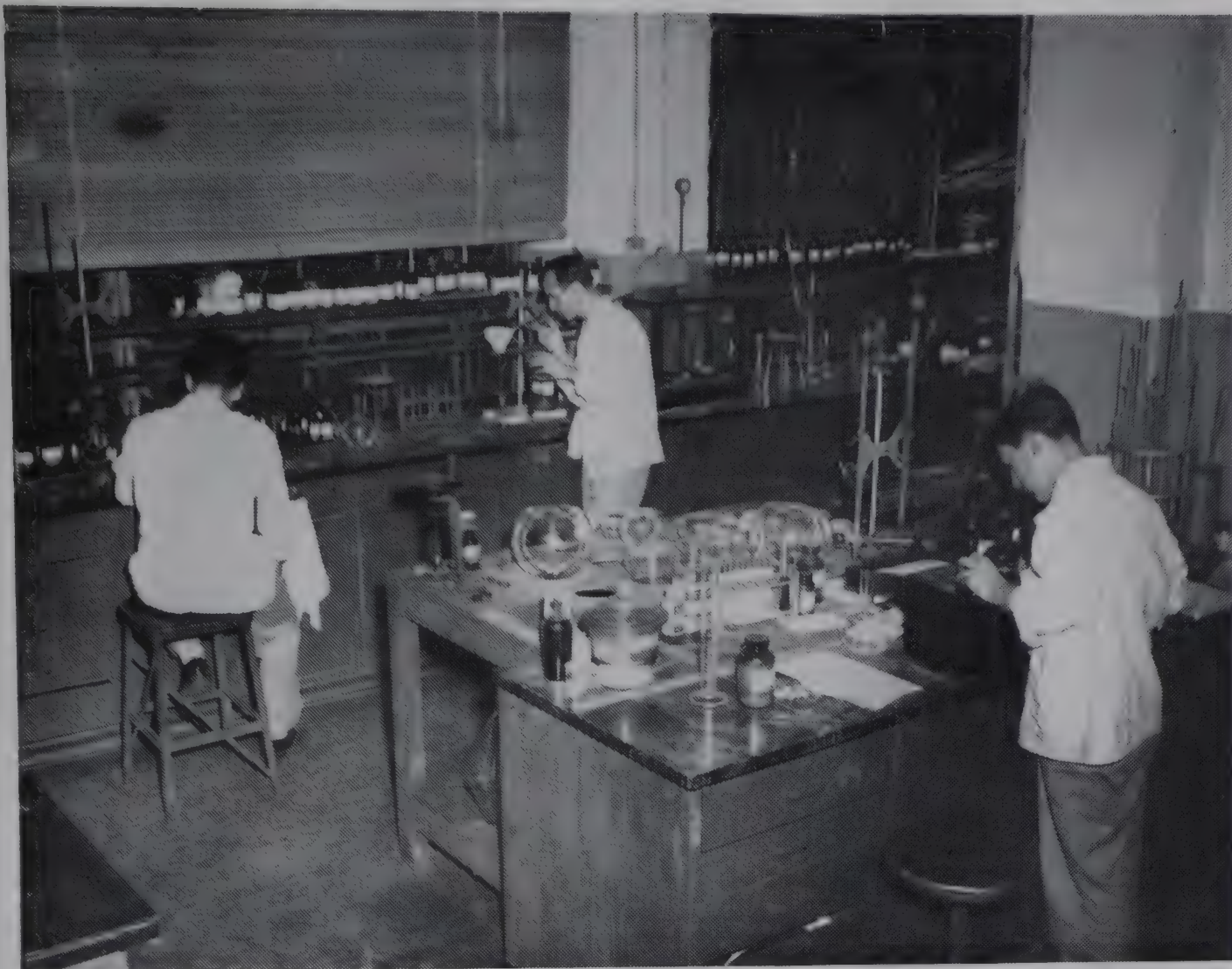
The preparation of potassium metaperiodate (KIO₄), Tested-Purity reagent, employs a two-step process in which (A) impure potassium iodate is oxidized by chlorine in an alkaline solution to potassium dimesoperiodate, and (B) the dimesoperiodate is converted to the meta compound by acidification with nitric acid. The raw materials for the preparation are: impure potassium iodate, obtained by crystallizing the mother liquor from the preparation of reagent potassium iodate; 45% aqueous solution of potassium hydroxide (Innis-Speiden, F.C. Grade); commercial grade chlorine; and technical grade nitric acid, 36° Bé. (approximately 52% HNO₃).

The solution for the oxidation step of the preparation is prepared by dissolving 50 pounds of impure potassium iodate in 60 gallons of city water in a Type 304 stainless steel 75-gallon kettle. It is rendered alkaline by the addition of 120 pounds of the potassium hydroxide solution, previously weighed out in three Type 304 stainless steel 10-gallon containers.

The solution is heated to 105° C. and, while still hot, is treated with an excess of commercial grade chlorine gas, sufficient to react with all of the potassium hydroxide. Control analyses for free alkali are run during the gasification of the solution to indicate the end point of the reaction. After chlorination, the process solution is again made alkaline by the addition of potassium hydroxide solution (about 10 to 15 pounds of 40% KOH). It is allowed to cool to room temperature and crystallize. The supernatant liquor is drawn off through a port in the bottom of the kettle. The oxidation reaction is described in the following equation:



The dimesoperiodate is removed from the kettle, weighed, and placed in a 60-gallon glass-lined steel kettle (11E). For each 100 pounds of the salt, 200 pounds of city water and 75 pounds of the commercial grade nitric acid are also added to the kettle. The process solution is digested at 105° C. to effect complete solution, and heating is continued in the open kettle until



Eimer & Amend Analytical Laboratory Where Final Check is Made on Reagent Grade Chemicals

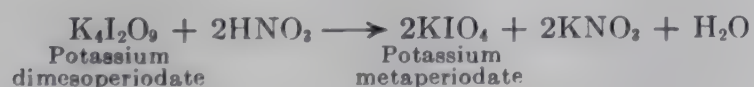
After checking, analyses are sent to printer for incorporation on labels

Weighing and Packaging

Because of the comparatively small amounts of chemicals packaged, most operations are manual



the volume is evaporated to about one half of the original. The acidification reaction is:



After cooling and crystallization, the mother liquor is drawn off through a port in the bottom of the kettle and stored in 10-gallon glass containers for introduction into subsequent batches before the acidification reaction. The crystals of potassium metaperiodate, which are obtained in 75% over-all yield, are removed from the kettle and centrifuged. The product is removed from the centrifuge, mixed with 2 gallons of distilled water in a stainless steel container, and centrifuged again to remove the excess acid on the surface of the crystals. Liquor from both centrifuging operations is recovered with the mother liquor. After drying for 18 hours in the tray dryer the metaperiodate crystals

are bottled in glass jars in 50-pound quantities for transfer to the analysis and packaging operations.

CUPROUS THIOCYANATE

At various times the plant is called upon to prepare a compound not in the company's regular line of reagents, for use as a purified raw material in a customer's pilot plant or product-application study. In such cases, the specifications are set by the purchaser and the method of preparation worked out by collaboration between the technical staffs of the customer and Eimer & Amend. The manufacture of cuprous thiocyanate on an order from a research agency of the French government 2 years ago is an example of the special type of preparation. The material was made for use as an active ingredient in marine antifouling paints. Specifications were that it be 99% plus in purity, have a uniform particle size (200 mesh) and contain less than 0.01% total acidity.

The raw materials for its preparation are commercial grades of copper sulfate, sodium bisulfite, and ammonium thiocyanate. The reaction involved consists of reducing cupric ion to the cuprous state by sodium bisulfite in the presence of ammonium thiocyanate to result in the precipitation of the desired cuprous thiocyanate. The precipitate is then washed, dried, and ground to meet specifications. The over-all reaction is as follows:



The three major ingredients in the reaction are made into solution separately and because of their commercial quality are filtered to remove extraneous solid material before they are introduced into the 240-gallon stoneware kettle (7E) where the reaction takes place.

The copper sulfate solution is made by dissolving 500 pounds of copper sulfate in 100 gallons of city water in a 100-gallon glass-lined, jacketed, steel kettle (11E). Solution is aided by heating to 70° C. before pumping the process material through the filter press to the reactor. The reducing agent is made into solution by dissolving 110 pounds of sodium bisulfite in 30 gallons of cold city water; it is then filtered and added to the reaction kettle. After these two ingredients are mixed intimately, by the use of an electrically driven agitator (10E), a solution of 154 pounds of ammonium thiocyanate in 30 gallons of city water is filtered into the same kettle. Agitation is continued for 5 minutes and control samples are taken to check the supernatant liquid for the presence of excess cuprous or thiocyanate ion.

The precipitated cuprous thiocyanate is allowed to settle for 18 hours and the supernatant liquid is decanted. The precipitate in the kettle is washed with city water until control samples of the wash water show less than 0.005% sulfate content and less than 0.001% sulfite content. The precipitated cuprous thiocyanate is discharged as a slurry through a port in the bottom of the kettle into 13-gallon rubber-lined steel containers and transferred for centrifuging. The cake is removed from the rubber-lined centrifuge by hand and placed in the dryer for 18 hours where it is desiccated at a temperature of 80° C. The product is recovered in an over-all efficiency of 95% and ground in a comminuting machine to a fineness of 200 mesh; it is then packed in 200-pound quantities in vinylite-lined fiber drums.

ANALYSIS AND PACKAGING

The reagents as packaged in bulk at the Edgewater plant are transported by truck to the main plant of the company in lower Manhattan. After delivery to the receiving department they are moved by service elevator to the fifth floor of the seven-story building for appropriate storage in a 4000-square-foot area equipped with four tiers of wooden shelves on steel supports. The bulk containers are stored by means of a portable elevator (1E). The storage area holds, at any given time, approximately 200,000 pounds of bulk-packaged technical, U.S.P., and reagent grade chemicals.

Upon storage, representative samples of the reagent grade and U.S.P. chemicals are taken by means of plastic samplers (6E) and placed in marked chemical sample bottles. After receipt in the analytical laboratory the reagent materials from both the Edgewater plant of the company and outside sources are analyzed according to company and A.C.S. specifications. The chemicals purchased under the designations U.S.P. and N.F. are analyzed for critical impurities.

If the analyses are satisfactory, an approval notice is submitted by the laboratory to the chemical inventory control department. When a stocking point is reached on any shelf chemical, the inventory department issues a packaging order to the head of the packaging department. This order includes:

1. Name and lot number of material to be packaged
2. Packaging instructions—that is, type of container and closure to be used and number of each type of package to be pre-



Storage Area, Eimer & Amend, New York

After receipt from Edgewater plant, bulk reagents are stacked by portable electric lift truck

pared (1-ounce, 0.25-pound, 1-pound, 5-pound, 25-pound, and 100-pound sizes)

3. Appropriate number of labels for the product, bearing name, formula, lot number, and lot analysis; labels are previously checked for accuracy against the master analytical record for analysis and lot number

It is significant to note the important role played by the analytical and packaging operations in the preparation of analytical reagents. Depending on the reagent, the quantity in which it is produced, the quality sought, and the purposes for which it is intended, the cost of analysis will vary from \$0.02 to \$3.00 a pound. Packaging costs, directly dependent on the quality, quantity, and nature of the product being packaged average about one fifth of the total cost of the preparation of a commercially available reagent. In some cases where intricate packaging is required, this cost may be as high as eight times that of the processing cost of the item itself.

FUTURE PROSPECTS

In the last decade there has been a marked increase in the use of bulk reagent grade chemicals as raw materials for pilot plant operations, product application studies, and small scale processes for the production of high purity compounds. This practice has arisen as a means of minimizing confusing or troublesome side reactions that may occur because of impurities present in many commercial grade raw materials. The use of reagent grade chemicals in such instances, in spite of their relatively higher cost, often represents an over-all economy because of the greater accuracy of pilot plant data or the improved quality of product that results.

To meet this growing nonlaboratory demand for reagent grade chemicals, manufacturers like Eimer & Amend have had to ex-

pand steadily the capacity of their facilities. This expansion of production volume has made it possible to keep reagent prices at low levels during a period when labor and equipment costs have soared.

Research and analytical laboratories, however, are still the major users of reagent grade chemicals. Although the con-

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Stock Room, Eimer & Amend, New York

Orders are assembled in basement stock rooms and sent by conveyor to main floor of plant

stantly changing nature of their work has at times shifted emphasis from some compounds to others, the over-all demand for reagents continues to rise and there is nothing in the foreseeable future to indicate a reversal of this situation. The trend toward instrumental methods of analysis has not diminished the need for reagents but instead has increased the variety and quality in which they are required. The growing practice of continuous wet method sampling in industrial processes will also tend to broaden the role of analytical reagents in instrumentation.

There is no doubt that the demands of analysis, research, and production have combined to make the manufacture of reagent grade chemicals an industry of prime importance to the nation's science and economy. To render maximum service the industry must be sensitive and adaptable to changing requirements and yet be assured of a profitable output of its staple items. For this reason competition in the future will become more highly developed than ever in the long and interesting history of this field.

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- (5E) *Ibid.*, pp. 1434-35, Tolhurst Centrifugals, solid curb type.
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LITHIUM and Its Compounds

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St. Louis Park, Minn.**

LIKE many other products of the chemical process industries, lithium and its compounds received their first great commercial boost from wartime needs. During World War II, lithium hydride, produced from metallic lithium, provided a convenient, lightweight source of hydrogen for the inflation of emergency balloons used to raise radio antennae from aircraft disabled at sea. By simple reaction with sea water, one pound of lithium hydride in a small canister generated about 45 cubic feet of hydrogen, obviating the need for cumbersome compressed gas cylinders as sources of hydrogen supply. Other less spectacular uses for lithium chemicals, such as the utilization of lithium hydroxide in Edison storage batteries, lithium chloride in welding fluxes for war materiel production, and lithium soaps in lubricating greases, contributed heavily to the upsurge in lithium chemicals output.

Lithium itself is anything but new; discovered in 1817 by the Swedish chemist August Arfvedson and isolated in metallic form a year later by Sir Humphry Davy, lithium remained commercially insignificant for about 70 years. Even then its uses in medicines and in the production of lithiated water provided outlets for only a tiny industry, and the development of more important uses was slow.

Within the last 15 years, improvements in methods of extracting lithium from its ores (3, 5, 9, 10, 14, 22, 23), coupled with great strides in the development of diverse commercial applications, have led to the establishment of a substantial lithium industry. Ceramics, lubrication, metallurgy, and air-conditioning now share in consumption of the constantly expanding output of lithium and its compounds (4, 7).

Data on world production of lithium compounds are not plentiful, but it is known that over 50% of the world's production of ores is centered in the United States (25). An indication of the lithium industry's growth in this country may be gleaned from U. S. Bureau of Mines estimates of the mining and shipment of lithium ores and concentrates as shown in Figure 1. These figures indicate the slow growth of the industry prior to World War II and show the influence of wartime demands, especially in the peak production year of 1944.

Table I provides an estimate of the probable distribution of lithium chemicals among consuming industries for 1951 (last 6 months), 1952, and 1953. Lithium carbonate is the most significant lithium compound currently produced, since it is widely used per se in the ceramics industry (6, 8, 20) and is also the starting material for a wide variety of other lithium chemicals, including metallic lithium.

The ability of carbonate-derived lithia to form low melting eutectics with various ceramic oxide compositions, often at very low lithia concentrations, makes it highly valuable in the porcelain enamel field (1, 6, 8). The hollow-ware industry in the United States has within the last few years become almost completely standardized on lithium-containing enamels, which allow: (1) decreased enamel firing temperatures with consequent reduction of warpage losses; (2) reduced firing time, resulting in increased production rates; and (3) improved thermal shock resistance, adherence, gloss, and stain resistance. For these uses, special ceramic compounds have been developed—lithium aluminate, metaborate, cobaltite, manganite, molybdate, silicate, titanate, zirconate, and -zirconium silicate are all in commercial production.

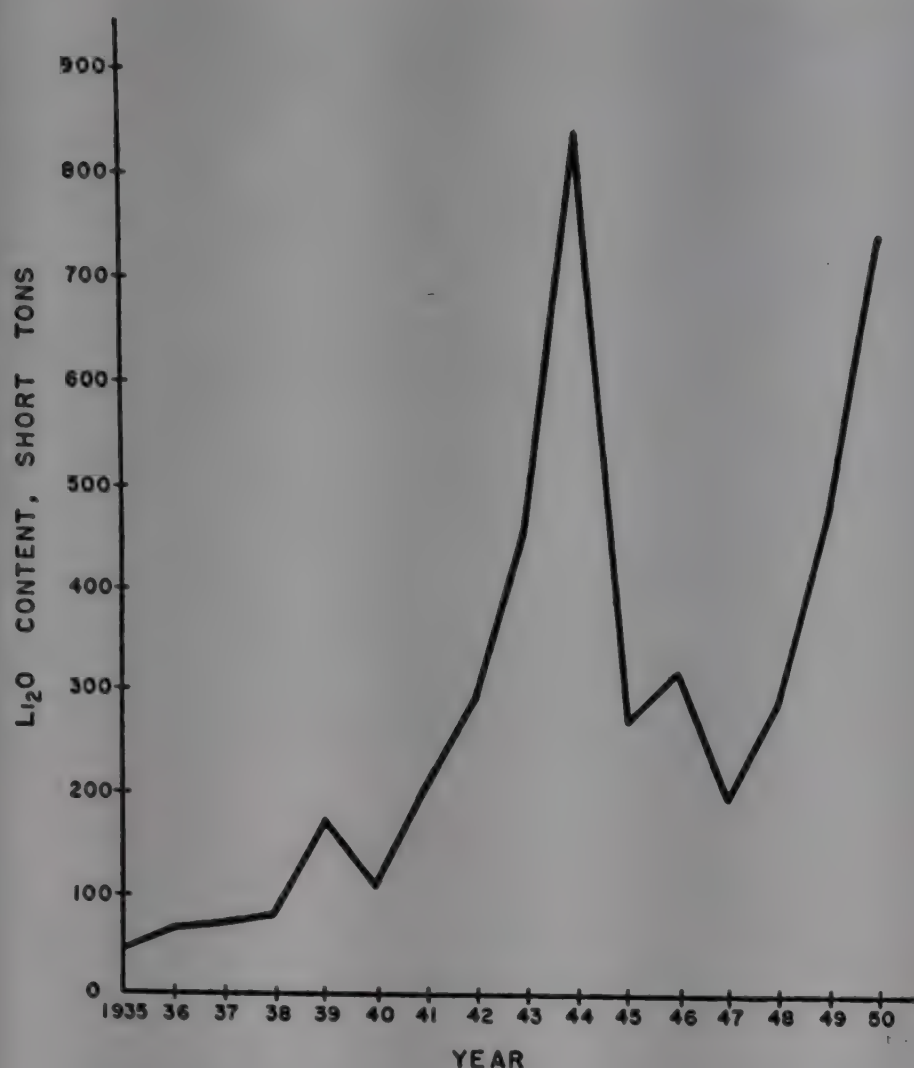


Figure 1. U. S. Production of Lithium Ores and Minerals—1935-50

Values for 1935-39 estimated from U. S. Bureau of Mines data (25)

Lithium hydroxide is a component of the electrolyte in alkaline batteries and has recently gained widespread use in the manufacture of lithium stearate for multi-purpose greases. These lubricants are efficient over the extremely wide temperature range of -60° to 320° F.

Lithium chloride has found application as a brine for air-conditioning systems (2) and is the starting material for the electrolytic production of metallic lithium. Lithium bromide, like the chloride, is useful in air-conditioning; lithium fluoride and lithium chloride are used in welding-rod coatings and in fluxes. Lithium amide is an important intermediate in the manufacture of anti-histaminics and other pharmaceutical products.

Metallic lithium shows some promise as a minor component in copper, lead, zinc, aluminum, and magnesium alloys, and by itself serves as an excellent deoxidizing and degassing agent for molten nonferrous metals. A small slug (about 0.005%) of metallic lithium added to a charge of molten copper, for instance, will effectively remove dissolved oxides and gases, to provide a more uniform casting with improved electrical conductivity (25). Because of their low density, the lithium products formed float to the surface and may be removed easily as slag.

A growing demand for lithium arises from the increasing use of lithium-containing organometallic compounds in Grignard-type reactions. The speed with which lithium has earned the attention of organic chemists is evidenced by the rapid increase in the number of research articles containing references to lithium compounds (16, 17); Table II reveals the extreme rate of increase within the past few years.

OCCURRENCE OF LITHIUM

The average lithium content of the earth's crust has been estimated at about 0.007% (15, 24). Of about 20 minerals known to contain lithium, only four—spodumene, lepidolite, amblygonite, and petalite—are known to occur in quantities sufficient to arouse commercial interest. The brine of Searles' Lake in California contains 0.02 to 0.03% lithium chloride by weight, and since 1938 sizable quantities of lithium have been recovered in the course of large scale extraction of potash, borax, and other salts from Searles' Lake brine (11). Lithium is recovered in this operation as a concentrate of lithium-sodium phosphate (Li_2NaPO_4) which has a lithium oxide content of about 20%.

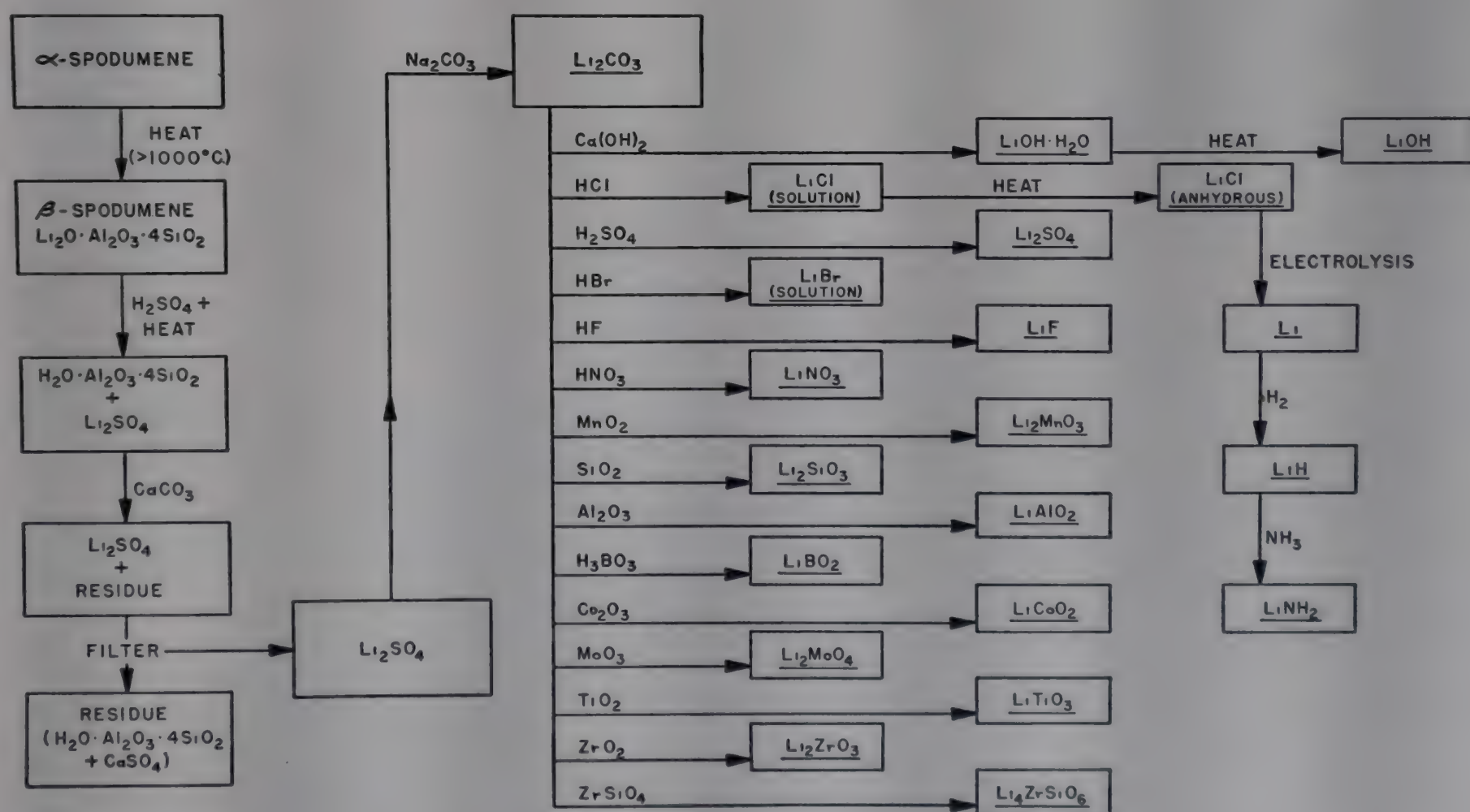


Figure 2. Derivation of Lithium Products from Spodumene

Spodumene, the most abundant lithium ore, has a lithium oxide content of 8.0% when pure, but existing ores as mined (18) usually contain only 1 to 3% Li_2O . Beneficiation by froth flotation (19) or hand-picking of crystals may increase lithia concentrations to 5 to 6% prior to extraction of the lithium content.

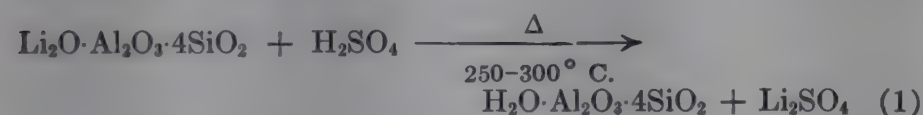
In its naturally occurring alpha form, spodumene is a hard mineral with a density of 3.15. When heated to 1100°C ., the alpha form is converted almost instantaneously to β -spodumene, which has a density of about 2.4 and is easily crushed to a very fine powder. The conversion of the mineral from the alpha to the beta form is the first important step in production of lithium chemicals from concentrated spodumene ores.

In the early days of the industry, lepidolite was the chief ore used: the mineral was decomposed by heating with concentrated sulfuric acid to yield a mixture of soluble lithium and other alkali sulfates with large amounts of aluminum sulfate. Extensive purification was necessary before the lithium could be recovered in a pure form. This same method is applicable to amblygonite but not to spodumene (4).

A notable improvement was the development of a base-exchange process (12, 26), in which the finely ground ore (lepidolite or spodumene) was heated with an excess of an alkali sulfate, usually the potassium salt. Potassium ions displaced lithium ions in the mineral, and a subsequent water leach yielded a solution containing lithium sulfate and the excess potassium sulfate used. Several variations of the base-exchange principle were developed in the years between 1900 and 1940, with varying degrees of success, but because of the relatively large proportions of reagents required, none proved economically feasible for large scale extraction of lithium from spodumene.

A process for recovering lithium from spodumene by subliming it as the chloride (10) attained commercial importance during the war. Widely known as the Bureau of Mines method, the chloride volatilization process was employed by Foote Mineral Co. and others in the large scale production of lithium salts using spodumene produced in great quantities by the Solvay Process Co. at Kings Mountain, N. C.

In the early 1940's, research at Metalloy Corp., now a division of the Lithium Corp. of America, led to the discovery of an entirely new method of recovering lithium from spodumene ore (5). Employing sulfuric acid as a source of hydrogen ions under critical conditions of time and temperature, the new method substitutes hydrogen for the lithium ions in β -spodumene, without changing the physical structure of the mineral in any visible way and without extracting any of the aluminum which is a part of the spodumene structure.



The water portion of the new aggregate is combined in the same manner as was the lithia component in the original spodumene. The water-soluble lithium sulfate, easily leached from the residue, becomes the raw material for conventional chemical processing to yield lithium in a wide variety of forms (Figure 2).

Armed with its new process, backed by extensive spodumene deposits, faced with the immediate military demand for tonnage quantities of lithium chloride as the starting material for the desired hydride, and assisted by government financing, Metalloy built a processing plant near Minneapolis, Minn., and at once undertook an extensive program which included production, research, and development. Through a stock transfer in 1947, Metalloy became a division of Lithium Corp. of America, now the only firm in the country devoted entirely to the production of lithium and its compounds.

At its Keystone, S. D., holdings alone, the corporation's developed ore reserves are sufficient for at least 20 years' operation at present rates, and its claims in the Cat Lake area of Manitoba (controlled by an affiliated corporation) have been proved to con-

tain at least 600,000 tons of 1.4% lithia. These deposits, plus others in Quebec and North Carolina, are sufficient for many years' production even at greatly expanded rates, and are so large that no further development work is contemplated at present. The actual mining is carried on principally by open-pit power shovel operations, although some deposits are worked through vertical shafts at depths of 200 feet or more.

Lithium Corp. was the first large producer to base its operations entirely on the use of spodumene, but several other companies now use spodumene as at least a partial source of lithium supply. Maywood Chemical Works of Maywood, N. J., has for many years produced lithium products from trona concentrates, and is currently utilizing spodumene to some extent in the production of free and combined lithium. Foote Mineral Co. of Philadelphia, Pa., has produced extensively from trona concentrates for several years, and has made use of several ores, including amblygonite and lepidolite as well as spodumene. Within the last year, Foote has vastly increased its ore holdings at Kings Mountain, N. C., and has doubled the capacity of its refining facilities at Exton, Pa.

ST. LOUIS PARK, MINN., PLANT OF LITHIUM CORP.

The manufacturing facilities of Lithium Corp. of America are housed, at present with considerable crowding, in ten small buildings located a short distance from Minneapolis, in the village of St. Louis Park, Minn. The rising demand for lithium and its compounds during the past few years has involved the company in a virtually continuous expansion program, the end of which is not yet in sight. The company's staff now includes fifty operating and maintenance personnel, three foremen, and eight technical and administrative personnel.

LITHIUM CARBONATE

Of the many processes conducted at the St. Louis Park plant, the most significant is the manufacture of lithium carbonate, since technical Li_2CO_3 is the largest in sales volume of all the company's products, and in addition, is the starting material for all its other lithium chemicals. These include metallic lithium,

TABLE I. PROBABLE DISTRIBUTION OF LITHIUM CHEMICALS^a, BY END USES—1951-53

End Use	Use, %		
	1951 (July-Dec.)	1952	1953
Ceramics (excluding glass)	31.0	36.0	39.0
Electronics	1.0	2.0	1.0
Lubricants	40.0	44.0	47.0
Storage batteries	10.0	4.0	2.0
Air-conditioning	5.0	4.0	2.0
Welding	4.0	3.0	3.0
Pharmaceuticals	4.0	3.0	2.0
Metallurgy	1.0	1.0	1.0
Export	4.0	3.0	3.0
	100.0	100.0	100.0

^a Employing lithium carbonate as the common denominator; each percentage figure represents the portion of lithium carbonate production that will be converted for a given use in a given year.

TABLE II. OCCURRENCE IN CHEMICAL LITERATURE OF RESEARCH ARTICLES BASED ON LITHIUM CHEMICALS—1910-51

Field	Period	No. Published Papers
Organolithium reactions	1910-47	223
	1948-49	136
	1950-April 1951	152
Lithium reductions	Prior to 1948	0
	1948-49	60
	1950-April 1951	212
Ceramics	1948	1
	1949	11
	1950	14
	1951 (Jan.-June)	12

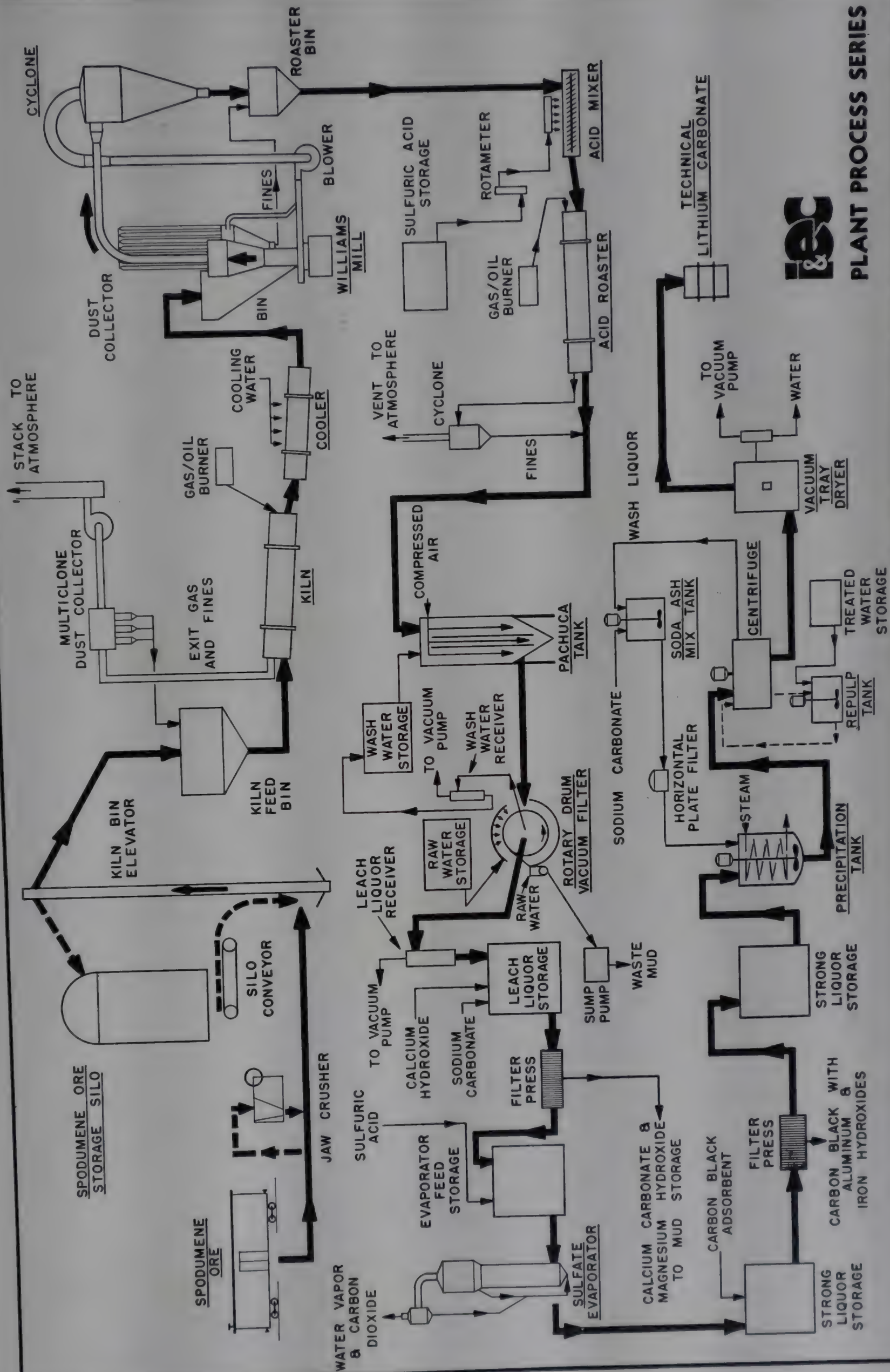


Figure 3. Flow Sheet for the Production of Lithium Carbonate from Spodumene Ores at St. Louis Park, Minn., Plant of Lithium Corp. of America

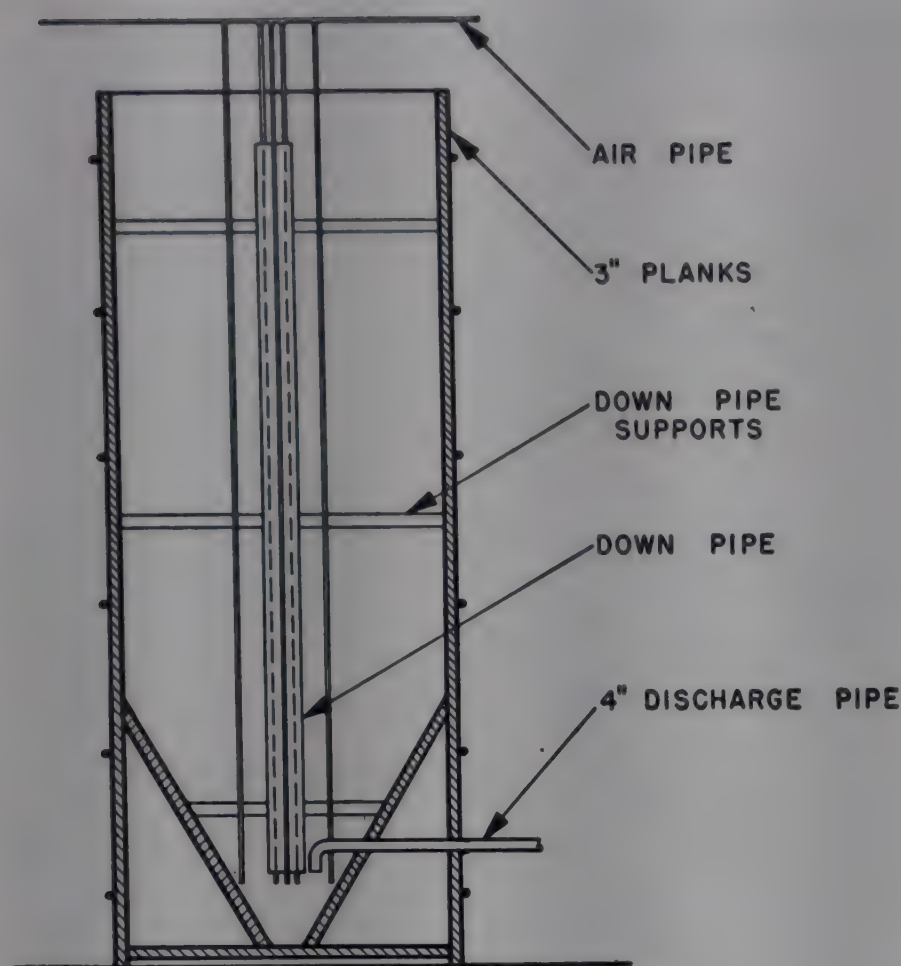


Figure 4. Pachuca Tank

lithium hydroxide, halides, hydride, and amide, and a variety of lithium-containing ceramic materials.

Figure 3 is a flow sheet for the production of lithium carbonate. The principal steps of the process consist of decrepitation and inversion of the ore, conversion of its lithium content to the sulfate, leaching of the sulfate from the gangue, and precipitation of the lithium as carbonate.

Spodumene ore, from which part of the gangue has been removed at the site of the company's mines in South Dakota, is shipped to the plant in boxcars. The ore as received generally contains 3 to 5% lithium oxide. Its size, 2 inches or less, makes it suitable for direct feeding to the decrepitation kiln. A 9 × 16 inch jaw crusher (10E) is available, however, for the preliminary breakdown of large lumps in occasional shipments of mine-run ore.

From the boxcars, the ore is transferred into the plant by a short, portable conveyor belt. Using a tractor-shovel (5E) inside the car, a load of about 50 tons can be transferred in about 2 hours. The portable conveyor belt discharges the ore to an enclosed bucket-type elevator with 4 × 10 inch buckets in a 14 × 42 inch sheet-iron shell. This elevator and others of the same type in use throughout the plant were designed by plant engineers and constructed to their specifications by a local manufacturer.

The bucket elevator is so situated that it can transfer ore from the boxcars either to the decrepitation kiln feed bin or to a large storage silo, which holds up to 4 carloads (200 tons) of spodumene ore. The same bucket elevator is used to transfer ore from the storage silo to the feed bin; a 12 inch × 10 foot conveyor belt connects the base of the silo with the base of the elevator.

The kiln feed bin, which holds about 65 tons of ore, feeds the ore at a controlled rate to a 12 inch × 8 foot belt conveyor which discharges into the kiln elevator. Ore is fed by gravity from the top of this elevator directly into the "cool" end of the decrepitation kiln. The kiln is 5 feet in outside diameter, 4 feet in internal diameter, and 40 feet long; it is rotated at approximately 1 r.p.m. It is fabricated of steel, lined for the first 20 inches with A. P. Green KX 99 superrefractory abrasion-resistant brick, and for the remainder of its length with Harbison & Walker Alamo high temperature firebrick. Depending on the moisture content of the ore in process, the rate of feed to the kiln may be varied from 1 to 2 tons per hour; the usual rate is about 1½ tons per hour.

Heat for the decrepitation of the ore is supplied by a burner (6E), which normally operates on natural gas; oil can be used if the gas supply is interrupted. The burner, equipped with a 32-ounce blower, supplies heat to the kiln at a rate of approximately 3,000,000 B.t.u. per hour. At the temperature of 1100° C. reached by the ore, decrepitation, with attendant conversion of the spodumene to the beta form, is 99 to 100% complete.

The flow of hot gases in the kiln is countercurrent to the flow of ore. The front section of the kiln, exposed to the gases at their maximum temperature, naturally suffers the severest heat effects; the first 3-foot section of firebrick lining is replaced, therefore, at intervals of about 6 months. The remainder of the kiln lining may be left intact for several years. A dust collector removes ore particles from the kiln exit gases, returning the solids by gravity to the kiln feed bin and discharging the gases through a stack to the atmosphere.

The ore leaving the kiln passes through a rotary cooler, which is an unlined steel cylinder, 30 inches × 26 feet, rotating at about 7 r.p.m. Cooling water flows over the outer surface of the shell at about 30 gallons per minute, lowering the temperature of the ore to 95° to 120° C. before discharge. Raw water for this purpose and for other operations in the plant is taken from a 425-foot well, with a 12-inch casing. The well pump (2E) is rated at 300 gallons per minute. The cooled ore is transferred by bucket elevator to a storage bin of about 25-ton capacity, from which it is fed to the Williams mill for comminution. A preliminary breakdown occurs in the kiln, so that the maximum size of particles entering the Williams mill is about 1 inch, and most of the ore is about 8-mesh or finer. However, further subdivision is necessary to ensure efficient acidification in the subsequent acid-roasting step.

In the Williams mill the ore is crushed between a large bull ring and a pair of heavy rollers, suspended from arms and rotating against the inner circumference of the ring. The bull ring is of manganese-molybdenum steel, surface hardened, and the rollers are of hard steel, with additional surface hardening. As the rollers wear down through abrasion, they are built up with Stoodly No. 21 hard surfacing welding rod.

A rising stream of air, supplied by the mill's auxiliary blower,

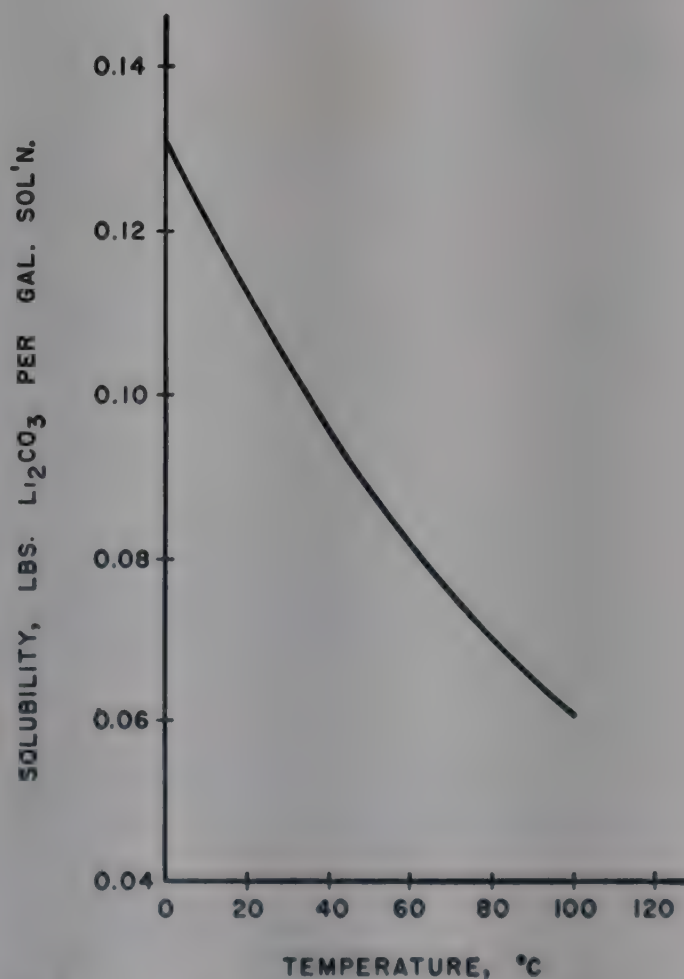


Figure 5. Solubility of Lithium Carbonate in Water (21)

carries the fine particles of ore overhead to a cyclone collector, while the heavy particles fall back into the mill for further grinding. The Williams mill is driven by a 25-hp. motor and has a capacity of about 4 tons of ore per hour, but the normal rate of operation is about 2 tons per hour. Air flow is controlled at such a rate that at least 70% of the ore collected in the cyclone will pass through a 200-mesh screen. A typical screen analysis of milled ore is given in Table III. The mill, the blower, the cyclone, and a dust collector for fines removal are all portions of an integrated system purchased as a packaged unit (11E).

TABLE III. SCREEN ANALYSIS FOR TYPICAL SAMPLE OF ORE LEAVING WILLIAMS MILL

Particle Size	Wt. %
+ 100 mesh	1.5
- 100 + 150 mesh	3.0
- 150 + 200 mesh	4.1
- 200 mesh	91.4

The ore from the Williams mill cyclone and dust collector is transferred by elevator to the roaster feed bin, which has a capacity of about 16 tons. From this bin, the finely divided ore is fed into a 12-inch horizontal screw conveyor, 10 feet long, where 66° Bé. (93%) sulfuric acid is added. The acid is distributed over the ore through the open top of the screw conveyor by means of a perforated pipe, of Type 304 stainless steel. The rate of acid feed, controlled to provide 35 to 40% excess acid above the theoretical requirement, is measured by a rotameter. The action of the screw, as it rotates at about 20 r.p.m. and conducts the ore to the acid roaster, suffices to mix the acid intimately with the ore. The rate of acid addition is about 500 pounds per ton of ore, adjusted in accordance with ore quality.

From the acid-mixing screw, the acidified ore is admitted to the roaster, where, at a temperature of about 250° C., the lithia content of the ore is converted to the sulfate. The acid roaster is an unlined mild steel rotary kiln 3 feet in diameter and 26 feet in length, rotating at 5 r.p.m. Heat is supplied by a gas-oil burner similar to that used on the decrepitation kiln, with the flow of hot gases concurrent in this case. The normal rate of ore flow through the acid roaster is about 2²/₃ tons per hour.

Lithium sulfate is next leached from the ore in either of two Pachuca tanks, which are connected in parallel and placed alternately on stream. The Pachuca (Figure 4) is a vertical wooden tank, 26 feet high and 9 feet in diameter, with a capacity of 8000 gallons. The tank bottom is conically tapered; in the center of the tank, along its vertical axis, an open-ended wooden tube, 12 inches square, extends from the top of the tank almost to the apex of the inverted cone at the bottom. When the Pachuca is filled with slurry, compressed air is forced through standpipes extending toward the bottom of the tank (both within and around the central tube) and allowed to bubble upward to the liquid surface. Agitation of the abrasive ore slurry is accomplished in this manner without the use of impellers, and settling of the solid particles is prevented.

About 11 tons of ore are handled per Pachuca batch; the charge is measured by volume change as the ore is delivered by bucket elevator into the leaching water. While the ore slurry is in the Pachuca, solid calcium carbonate is added in an amount sufficient to neutralize the excess sulfuric acid introduced in the acid mixer. About 1500 pounds of calcium carbonate are required for the neutralization, which raises the pH to about 6 or 6.5. The neutralization and leaching step is finished about one half hour after the addition of ore to the Pachuca is complete.

The neutralized Pachuca batch next flows by gravity to the vacuum drum filter (7E), which separates the leach solution from the remaining ore gangue mud. An 8000-gallon Pachuca batch is filtered in slightly over 2 hours. During the cycle on the filter,

the mud is given one wash with raw water; this wash water is recovered and stored in an 8000-gallon tank, from which it is withdrawn to be used as leach water for the next Pachuca batch. The mud as it is scraped from the filter contains about 30% water and is discharged at about 6 to 6.5 tons per hour. The loss of soluble lithium through the filter mud is normally well below 1% of the total contained lithium in the starting ore. The discharged mud enters a screw conveyor, where it is reslurried with raw water; the slurry is removed by a sand pump (3E) to a low, swampy area on the company's property.

The strong leach liquor from the drum filter, containing about 10% lithium sulfate, is pumped to one of two 11,000-gallon leach liquor storage tanks, where the pH of the solution is raised to 12 by the addition of hydrated lime. At this point, the small amount of contaminating magnesium is precipitated from solution as the hydroxide. About 100 pounds of soda ash are then added for each 1000 gallons of solution, to precipitate the calcium ions as the insoluble carbonate. When laboratory control tests indicate that precipitation of both magnesium and calcium is complete, the solution is pumped through a 24 × 36 inch plate-and-frame filter press (8E) and into the 11,000-gallon evaporator feed storage tank. The mud from the filter press is stored, and periodically it is repulped and returned to the Pachuca as a separate digest in order to recover the last traces of lithium sulfate.

In the evaporator storage tank, sulfuric acid is added to adjust the pH to 7 or slightly higher, causing precipitation, as hydroxides, of the small amounts of iron and aluminum present. The traces of aluminum come from the ore, whereas the iron is picked up from steel pipes and evaporator tubes. Subsequent loss of carbon dioxide in the evaporator results in a moderate increase in pH. The single effect evaporator for concentrating the sulfate has 180 tubes, 2 inches × 10 feet, and removes water at the rate of 285 gallons per hour. Control over the evaporator's performance is maintained through frequent measurements of specific gravity.

The concentrated liquor from the evaporator, now containing about 20% lithium sulfate, is collected in an 11,000-gallon storage tank, where a small amount of decolorizing carbon black is added. The carbon black is removed, along with the iron and aluminum hydroxides, as the liquor passes through a 24-inch plate-and-frame filter press (8E) and into another strong liquor storage tank of 11,000-gallon capacity.

The strong liquor is pumped next to a smaller tank equipped with an agitator and an internal steam coil, where the lithium is precipitated from solution as the carbonate. Soda ash is used as the precipitant; a solution containing 2.75 pounds of soda ash per gallon of solution is prepared in an auxiliary mixing tank and pumped through a small clarifying filter (9E), into the precipitation tank. Since the solubility of lithium carbonate decreases with increasing temperature (Figure 5), the batch temperature in the precipitating tank is kept relatively high (about 90° C.) to ensure maximum precipitation. Two precipitating tanks, constructed of Type 304 stainless steel, are used in parallel.

The lithium carbonate slurry is pumped to a centrifuge (4E), which separates the carbonate crystals from the mother liquor. The centrifuge, including the discharge hopper, is also of Type 304 stainless steel. The crystals are removed and repulped in a small stainless steel tank, using de-ionized water with an electrolyte content of less than 1 p.p.m. as sodium chloride, and returned to the centrifuge. The final wringing yields about 250 pounds of lithium carbonate per basket (dry basis), containing about 10% moisture. Each centrifuge basket of carbonate is carried through separately in this way before a new centrifuge charge is withdrawn from the precipitation tank. The "wet" carbonate from the centrifuge is discharged into fiber drums for transfer either to the dryer, for carbonate which is to be sold as such, or to the other units within the plant if the carbonate is to be converted to other lithium chemicals. Current production of carbonate by Lithium Corp. is at the rate of about 6000 pounds per day.

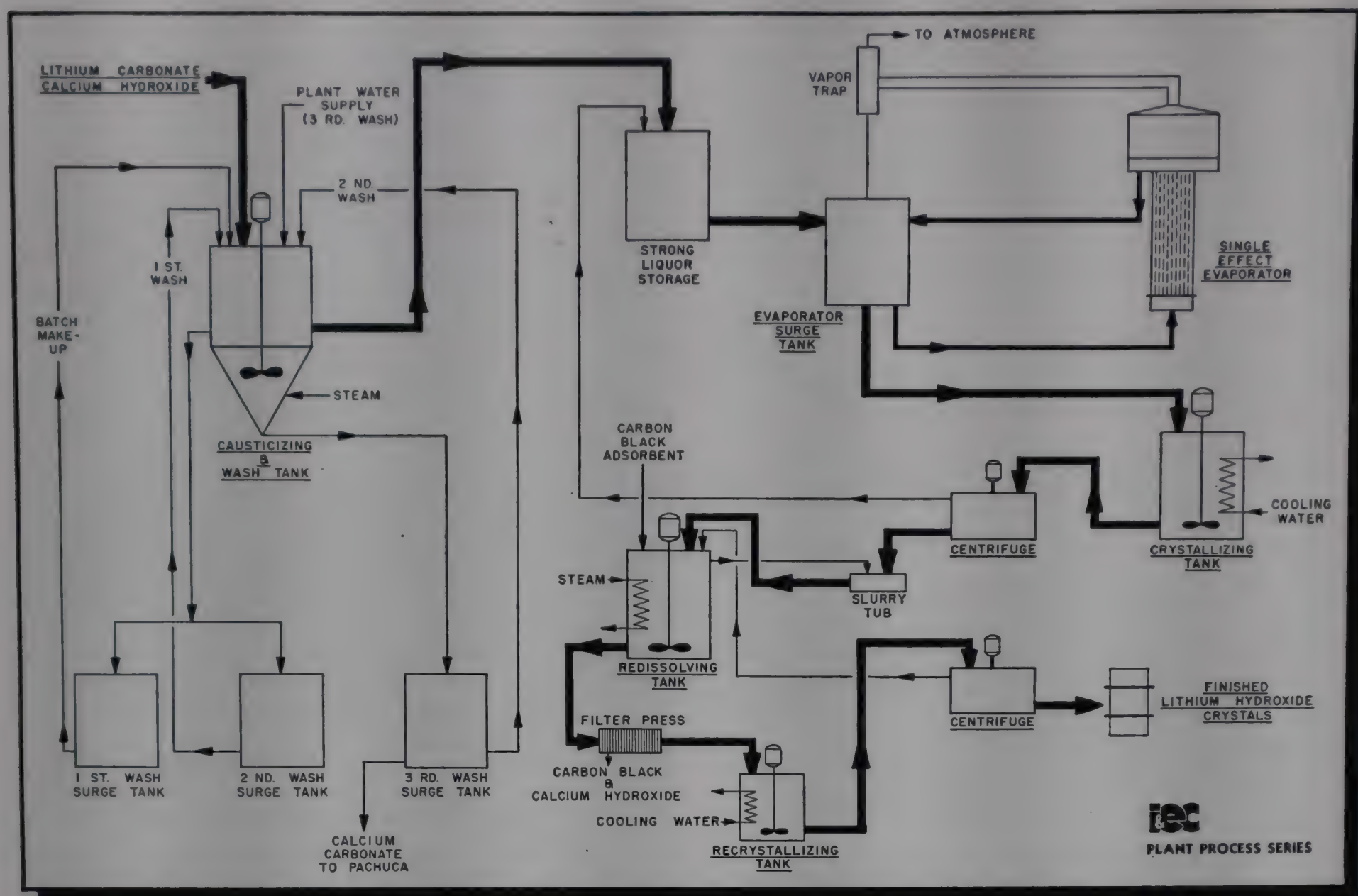


Figure 6. Flow Sheet for the Production of Lithium Hydroxide from Lithium Carbonate

The dried product sold as technical lithium carbonate is used entirely in ceramic applications, with the major portion going into low temperature porcelain enamels. To produce the dry technical grade, wet carbonate is transferred to a vacuum dryer (1E), which holds a total of 1200 pounds of carbonate on nineteen shelves. A vacuum of 20 to 25 inches of mercury is maintained during the drying cycle, which lasts about 4 hours.

Metalloy's lithium carbonate is used as the starting material for all its other lithium chemicals, including metallic lithium. Specifications and typical analyses for several of these materials are given in Table IV. Wet carbonate is the starting material for production of lithium hydroxide, halides, sulfate, nitrate (via the hydroxide), metal (via the chloride), hydride (via the metal), and amide (via the hydride). Dry carbonate is required for the production of Metalloy's own line of lithia-containing ceramic compounds, which are prepared by heating lithium carbonate with the appropriate oxides of other metals.

Lithium Hydroxide

In the manufacture of lithium hydroxide, second largest in volume among Lithium Corp.'s products, wet carbonate and hydrated lime are mixed in the ratio of 100 pounds of lithium carbonate to 105 pounds of calcium hydroxide, in either of two 875-gallon causticizing tanks equipped with agitators. The ratio used is equivalent to approximately 5% excess of lime. The amount of total solids charged depends on the quantity and concentration of the make-up solution—a wash solution with a low concentration of lithium hydroxide from a previous batch. Sufficient lime and carbonate are added to raise the concentration of lithium hydroxide (LiOH) to 0.3 pound per gallon. A typical preparation would call for 260 pounds of lithium carbonate (dry basis), 275 pounds of calcium hydroxide, and enough make-up solution with an initial concentration of 0.09 pound per gallon to

make a 725-gallon batch. The reactants are slurried and heated to boiling by means of steam, in order to secure the highest practical concentration of lithium hydroxide in the solution. When reaction is complete, the slurry is allowed to settle and the clear liquor is decanted to a 2500-gallon strong liquor storage tank.

As indicated in the flow sheet for lithium hydroxide production (Figure 6) the residual calcium carbonate mud is washed free of lithium hydroxide in a three-stage countercurrent decantation process. The clear liquor decanted from the first and second stages is advanced to separate 2500-gallon surge tanks. The mud slurry from the final stage, substantially free of lithium hydroxide, is pumped to a 3750-gallon surge tank, from which the settled mud is periodically returned to the carbonate process for use in the Pachuca operation.

Typical lithium hydroxide concentrations of the effluent strong liquor and wash solutions are:

	Lb./Gal. of Solution
Strong liquor	0.24–0.30
First wash	0.07–0.10
Second wash	0.03–0.05
Third wash	0.015–0.03

The strong liquor from the causticizers is concentrated to the saturation point (1.39 pounds per gallon at 100° C.) in a vertical tube, single-effect evaporator. The evaporator, which discharges approximately 2400 gallons of concentrated liquor in a 12-hour period, contains 74 tubes, 1 1/4 inches × 10 feet, and is supplied with steam at 30–40 pounds per square inch; the discharge rate is equivalent to the evaporation of 280 gallons of water per hour. Operators make frequent checks on the concentration of the liquor during evaporation.

The concentrated solution from the evaporator is next pumped

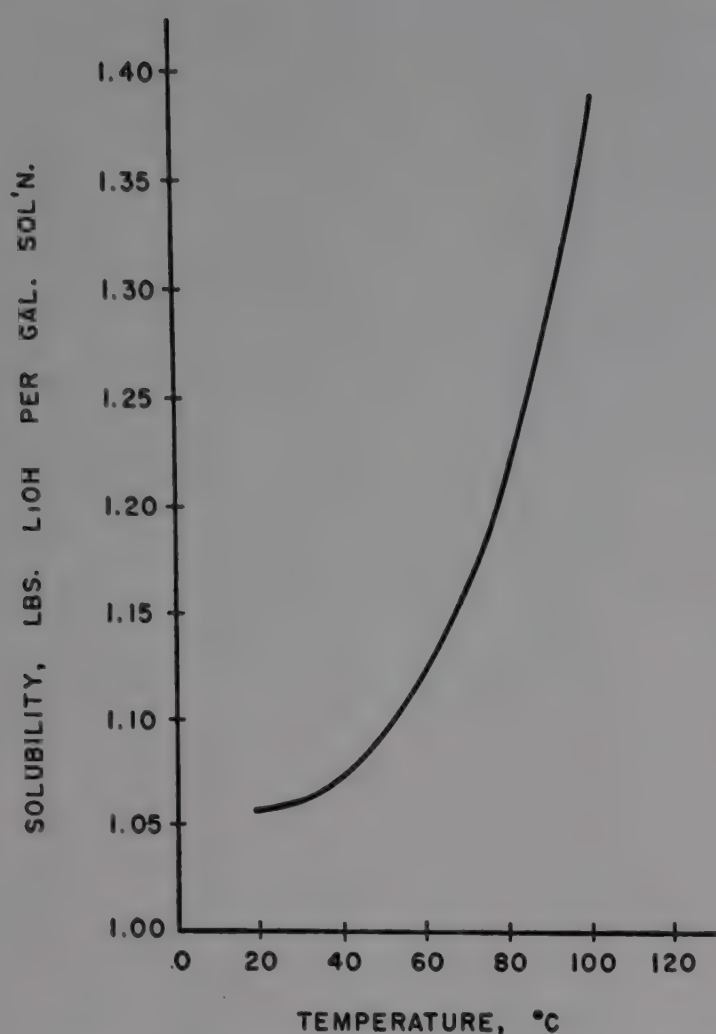


Figure 7. Solubility of Lithium Hydroxide in Water

Data in part from International Critical Tables (13)

to the crystallizer. This unit consists of a 2500-gallon steel tank fitted with internal coils made from 745 feet of 1½-inch tubing. With circulating water as the cooling agent, the concentrated hydroxide solution is cooled from an initial temperature of near 100° C. to about 40° C. (Cooling below the 40° level does not appreciably increase the yield of crystals, as indicated by Figure 7.) The hydroxide separates from solution as the monohydrate. When the temperature of 40° C. is reached, the agitated slurry of crystals and solution is pumped to the centrifuge (4E). The crystals are given a 15-minute wring in the centrifuge, and the mother liquor is returned to the evaporator storage tanks. Between 1300 and 1400 pounds of first crystals are separated from each 2400-gallon batch of concentrated solution. Cooling and centrifuging require about 8 hours.

The first crystals contain some lime and other impurities. To effect purification, the first crystals are redissolved in a 2500-gallon tank and are filtered and recrystallized. The liquor used for redissolving the first crystals is obtained from the previous recrystallization batch. Enough first crystals are added to this liquor to ensure saturation of the hot solution (1.39 pounds of lithium hydroxide per gallon). A small quantity of carbon black is added for color removal, and the solution is pumped through a small plate-and-frame filter press to the two 875-gallon recrystallization tanks. The filter removes the carbon black and the insoluble lime. Like the large crystallizer tank where the first crystals are formed, the two recrystallizers are fitted with cooling coils and agitators. To prevent contamination of the final product they are constructed of Type 304 stainless steel. The filtered solution is cooled to 35° to 40° C. by circulating well water, and the finished crystals are removed by centrifugation. In the recrystallization operation about 1700 gallons of solution are cooled per batch, yielding nearly 1000 pounds of product as the monohydrate. The total capacity of the hydroxide plant is 2400 pounds of monohydrate crystals each 24 hours.

Lithium Chloride

For the production of lithium chloride wet lithium carbonate as it comes from the centrifuges, containing from 8 to 12% moisture,

TABLE IV. SPECIFICATIONS AND TYPICAL ANALYSES FOR COMMERCIAL LITHIUM COMPOUNDS

	Impurities, %	
	Maximum	Typical Production Sample
LITHIUM CARBONATE, TECHNICAL		
Moisture (loss at 110° C.)	0.50	0.01
SO ₄ ⁻⁻	0.50	0.35
CaO	0.05	0.04
Na ₂ O + K ₂ O	0.30	0.18
Fe ₂ O ₃	0.005	0.003
Heavy Metals	0.002	<0.001
Chlorides	0.01	<0.005
LITHIUM HYDROXIDE MONOHYDRATE^a		
Cl ⁻	0.003	0.002
NaOH	0.05	0.01
SO ₄ ⁻⁻	0.05	0.02
Fe ₂ O ₃	0.005	0.001
CaO	0.08	0.05
CO ₂	0.20	0.10
Insolubles	0.01	0.005
LITHIUM CHLORIDE, TECHNICAL		
Moisture	1.00	0.60
Alkalinity as Li ₂ CO ₃	0.10	0.06
SO ₄ ⁻⁻	0.01	0.01
CaCl ₂	0.15	0.10
NaCl + KCl	0.50	0.40
Fe ₂ O ₃	0.006	0.003
BaCl ₂	0.01	0.01
Insolubles	0.025	0.01
LITHIUM METAL		
Na	..	0.6
K	..	0.01
Ca	..	0.02
N	..	0.06
Fe	..	0.001

^a Specified minimum assay as LiOH, 53.5%; typical production sample, 55.0%.

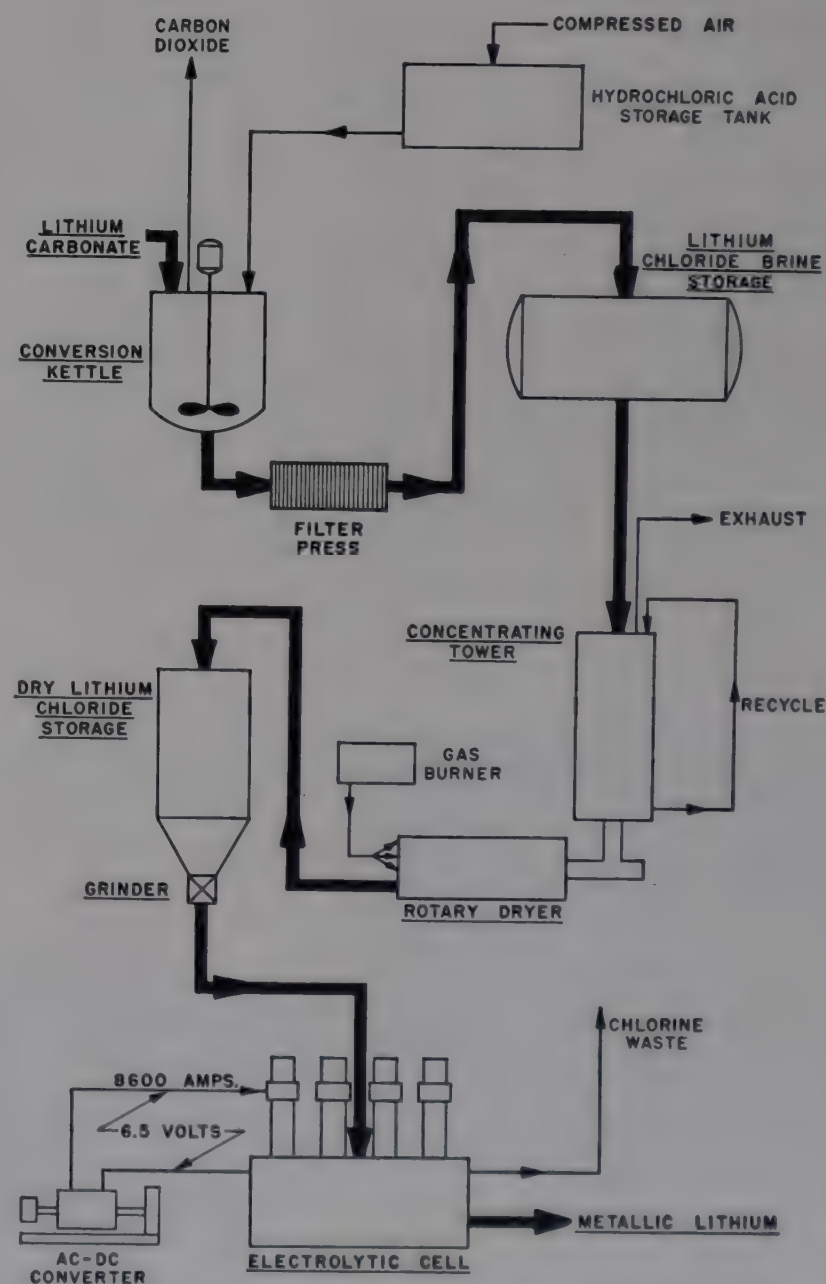


Figure 8. Flow Sheet for the Production of Lithium Chloride and Metallic Lithium

is treated with muriatic acid (31% HCl) in an 1800-gallon rubber-lined reaction kettle equipped with a rubber-coated agitator and rubber-lined outlet valves. In each batch about 3500 pounds of wet carbonate are added to 1020 gallons of acid, giving a brine of 1.180 to 1.195 specific gravity. This solution contains approximately 3 pounds of lithium chloride per gallon. The carbon dioxide formed during the reaction is removed through an exhaust system.

When all the carbonate has been charged, a slight excess of acid is added, and the brine is agitated for one half hour. The small sulfate content of the brine is then precipitated by the addition of barium chloride; when control tests indicate that precipitation is complete, any excess acid is neutralized with lithium carbonate. Since users of lithium chloride prefer to receive it in a slightly alkaline state, lithium hydroxide is added until the alkalinity of the brine is 0.01 *N*. Any excess barium chloride is removed with sulfuric acid. The brine is filtered through a plate-and-frame filter press and transferred to a 5000-gallon rubber-lined storage tank. Each conversion cycle is completed in about 8 hours.

Dryer Operation. A small portion of the lithium chloride produced is sold as a 40% brine, but demand for the dry salt is far greater. Dry solid lithium chloride is produced from the brine by a concentrating tower and a rotary dryer in series. Brine from the storage tank is pumped at about 40 gallons per hour to the top of the ceramic-lined and -packed tower. Hot exit gases from the rotary dryer pass up through the packed tower and concentrate the brine as it flows down over the packing. The brine is collected in a circular trough at the bottom of the tower; a portion is recirculated to the tower, while the remainder flows into the feed end of the ceramic-lined rotary dryer. Since the brine is highly corrosive, rubber pipe is used for the recirculating lines. The rate of brine recirculation is keyed to the heat output of the burner, so that solidification does not take place in the tower but does occur in the dryer. At the point in the dryer where brine begins to solidify, a ring of dried chloride several inches thick forms on the walls. As the paste dries out it spills over the top of this ring and moves as a granulated solid toward the discharge chute at the end of the drum.

About 120 pounds of lithium chloride can be dried to a moisture content of less than 1% during each hour of operation. Since the chloride as it leaves the dryer is somewhat lumpy, it must be ground before packaging. The lumpy material is stored in a closed, Type 302 stainless steel hopper which holds up to 3500 pounds of chloride; when the hopper is full the chloride is ground through a hammermill, fitted to the bottom of the hopper. Equipped with a $\frac{3}{16}$ -inch screen, the mill produces chloride particles ranging in size from 8-mesh downward.

Lithium chloride is extremely corrosive, especially in the presence of water. Since it is also very hygroscopic, it presents serious corrosion problems. Whenever the dryer is shut down, therefore, all exposed steel surfaces in the drying room must be thoroughly washed and steamed to remove the highly corrosive salt.

Figure 8 is a flow sheet for production of lithium chloride and from it, metallic lithium.

Lithium Metal

Metallic lithium is produced by the electrolysis of a fused eutectic mixture of lithium chloride and other alkali salts. The housing of the electrolytic cell consists essentially of a steel box 4 × 6 feet across and 3 feet deep, constructed of 1-inch boiler plate and heat treated after fabrication. The box is supported in an outer brick-lined shell in such a way that flames from gas burners built into the outer shell impinge on the bottom of the inner box to keep the electrolyte in the molten state. To prevent deterioration of the cell walls, the inner box is provided with a liner of carbon blocks sealed with a carbonaceous cement.

Four graphite anodes, each 8 inches in diameter and 6 feet

long, are supported from above the cell and extend downward into the electrolyte bath. The cathodes are of steel. An exhaust fan maintains a slight negative pressure within the cell and discharges by-product chlorine fumes through a 60-foot stack to the atmosphere. The amount of chlorine discharged is not sufficient to create an atmospheric pollution problem.

Power is supplied from a motor-generator set installed just outside the cellroom. The set converts 440-volt alternating current into 6-volt direct current, with an efficiency of about 80%. Under normal operating conditions the cell draws 8600 amperes at 6 to 6.5 volts.

When the cell is in operation, lithium metal forms in the bath as small droplets about the size of marbles. These rise quickly to the surface. The cell is so designed that natural circulation in the bath directs the droplets of molten metal to the front of the cell, where they merge into a pool; a thin film of molten salts forms on the surface of the metal and shields it against atmospheric attack. This protection is a fortuitous property of the cell-bath composition; no special materials are needed to provide the protective film. Periodically an operator, using a special ladle, skims off the layer of molten lithium. The metal is allowed to cool in the ladle to a temperature below the melting point of the cell bath but above the melting point of the lithium. Any molten salt which has been picked up in the skimming operation thus solidifies in the ladle, and the metal can be poured into ingot molds virtually without contamination from the salt. Approximately 90 pounds of metallic lithium are produced in each 24-hour period.

The cell is operated on a 24-hour, 7-day basis, as is the ore-preparation department. (Other portions of the plant are operated 6 days per week.) The cell is usually run continuously for about 3 months and is then shut down and drained for relining. Under normal conditions one set of anodes lasts throughout a 3-month period. Anodes can be replaced while the cell is operating, but it is more convenient to replace them when the cell is shut down. The cell's efficiency varies somewhat throughout the length of a run, depending on the condition of the anodes. As the anodes are eaten away, the voltage required for a given amperage is increased. When the voltage reaches a predetermined upper limit, the anodes are lowered into the bath far enough to reduce the required potential once more to 6 volts.

Remelting and Handling the Metal. Much of the metal produced by the cell is remelted and cast into various size ingots. In remelting, the last traces of nonsoluble impurities in the metal are separated. The remelt furnace consists of a pressed steel pot, set into an electrically heated furnace. Ingots from the electrolytic cell are placed in the steel pot, melted, and held at a temperature somewhat above the melting point of 186° C. The nonsolubles either float to the top of the metal, where they can be skimmed off, or sink to the bottom of the pot where they are removed during a shutdown. The pot is enclosed; a blanket of oil vapor above the surface of the molten lithium prevents atmospheric oxidation or nitriding.

Through a special spout set into the side of the remelt furnace, the molten lithium is tapped off into the proper molds. The size and type of mold used depends on the end use for which the lithium is intended. The ingots vary in size from a small biscuit-shaped casting weighing 0.2 pound to the larger tapered "cylinders" weighing 2.0 pounds. The new ingots are immediately sprayed with oil to prevent any attack by the atmosphere. As molten metal is removed, additional crude ingots are added to the furnace, where automatic controls maintain a constant temperature.

In handling molten lithium, care must be taken to prevent its coming in contact with any moisture. Occasionally fires do break out, and they can be effectively extinguished only by smothering with a suitable material. Of all the substances which have been tried for smothering lithium fires, lithium chloride is the only one found suitable to date. Nearly all other materials tested react with the lithium in varying degrees of vigor.



Unloading Boxcar



Williams Mill



Acidification

Spodumene Ore Operations

For its many end uses, lithium is extruded into rod and wire of various sizes. For this work a 150-ton hydraulic press is used; the wire, extruded at about 60 feet per minute, is fed through a bath of molten petroleum jelly which coats the metal with a thin protective film. Rods are cut to set lengths, corresponding to chosen weights, and dry-packed in airtight cartridges.

Lithium Hydride and Amide

Although the market for lithium hydride has dropped considerably since the end of the war, the product is still significant since it is the primary raw material for lithium amide production. In producing the hydride, pure metallic lithium is melted under high vacuum and is allowed to react with hydrogen. The initial evacuation, to a pressure of 1 mm. of mercury or less, is necessary to prevent reaction between the hot metal and oxygen, nitrogen, or moisture from the atmosphere. About 70 pounds of lithium are melted in each charge to the electrically heated hydride furnace. Hydrogen is admitted slowly until a positive pressure of about 5 pounds per square inch is built up. The reaction is highly exothermic, and once begun requires no further external heat to maintain the required temperature. The walls of the hydride furnace bowl are tapered toward the bottom, so that the hydride can be conveniently removed as a single mass when reaction is complete.

For the manufacture of the amide, lithium hydride is crushed, spread on shallow trays, and heated in a gas-fired oven in an

atmosphere of ammonia. The hydrogen evolved is burned at the exit end of the oven, and the exhaust gases are discharged through a stack. The amide has found wide acceptance as an intermediate in the manufacture of pharmaceuticals—primarily the antihistamines—because of its stability advantages over sodium amide and other intermediates.

Lithium Bromide

The production of lithium bromide is analogous to that of the chloride, except that all the bromide is shipped as a brine and none as a dried solid. Technical hydrobromic acid, purchased in carboys as a standard 45% aqueous solution, is allowed to react with lithium carbonate in 1250-gallon batches in the rubber-lined unit used for chloride production. The pH of the resulting weak lithium bromide brine is adjusted through carbonate addition, until it is slightly alkaline; lithium hydroxide is then added until the solution is about 0.01 *N* with respect to hydroxide. The slightly basic solution is filtered into a concentrating tank, where steam heat is used to concentrate the brine to 55% strength. This brine, which finds its primary use in air-conditioning applications, is shipped in 55-gallon steel drums holding about 700 pounds of solution. Corrosion problems are minimized in the handling of the bromide brine, since drying is not required, and the salt solution remains within the enclosed, rubber-lined system until shipment is made.

Leach Liquor Tank



Lithium Carbonate Operations

Acid Roaster



From Centrifuge to Dryer



Ceramic Raw Materials

The ceramic compounds manufactured by Lithium Corp. are all produced by the same general method, differing only in the temperature at which the mixed oxides are kilned. A dry blend of lithium carbonate with the appropriate metallic oxide is heated in a small kiln, to a temperature substantially below that required for fusion or decomposition. One kiln is used for the production of colored ceramics, such as the manganite and cobaltite; a separate kiln is reserved for the white ceramics.

FUTURE PLANS

The rapid growth in demand for Lithium Corp. products during the past few years has required a number of make-shift installations wherever space could be found. Sometimes this has meant the adoption of practices which were known to be inefficient but which were necessary as temporary expedients. Plans are now under way at the St. Louis Park plant for consolidation of the several processes into more distinct and efficient units; the ultimate goal is to confine each process, as nearly as is practicable, within its own separate building.

High on the list of projects for improving efficiency is the construction of a system for the bulk-handling of soda ash. The new system will include a 130-ton storage bin near the plant's railroad siding, and mixing tanks from which dissolved soda ash can be pumped as needed to any part of the plant. The installation will eliminate entirely the manual handling of 100-pound bags.

The lithium chloride drying process currently in use has not proved satisfactory, since it is not easily controlled and does not yield the chloride in the most desirable physical form. Development work on a new drying system is expected to lead to a different and more efficient chloride drying system, which will yield the salt in a free-flowing granular or crystalline form.

Through the installation of new equipment where needed and the improvement of equipment and methods now in use, it is expected that bottlenecks can be eliminated in the chemical processing areas, approximately doubling throughput rates in these units and allowing utilization of the ore-refining facilities at their maximum capacity. The economics of over-all plant operation would thus be substantially improved.

A large flotation unit now under construction at the site of the company's South Dakota spodumene mining operations is expected to begin operation during the first quarter of 1952 and will provide an additional and significant increase in production of lithium chemicals. The flotation concentrate, consisting of particles that will pass through a 50-mesh screen, will have a lithia content of 5 to 5.5%, effectively boosting the capacity of the St. Louis Park extraction facilities by about 50%.

With this expansion program, precautionary measures will be added for the further protection of employees and of residents in the plant area. For example, although the amount of waste chlorine now discharged to the atmosphere is below the nuisance limit, an absorption system will be added to make certain that increasing production will not lead to atmospheric pollution problems.

The horizon for lithium and its compounds is growing broader and brighter. The demand for lithium carbonate alone has become so great that current capacity is insufficient to maintain supply-demand balance. The sky-rocketing interest in and demand for lithium compounds in all-purpose greases is actually somewhat disturbing in the light of limited production facilities now available. It has been estimated recently that lubricant demands of the military alone, if fully satisfied, could consume the entire present production of extracted lithium in the United States. Even an approach to such a status would seriously upset the ceramics industry, which leans more and more on lithium compounds to maintain its competitive position.

Already the boosts in lithium output have lowered costs sufficiently to give lithium compounds an economic advantage in

many uses in which they were once entirely outclassed pricewise. An example is the production of low temperature glazes, in which lithium can effectively replace lead. Contemplated expansions in plant capacity and improvements in operating efficiency will undoubtedly alter the economics of other potential lithium applications. The stimulation of research into entirely new fields has already accounted for significant changes in demand and will undoubtedly give rise in the future to additional large outlets for lithium and its compounds.

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Processing Equipment

- (1E) Buffalo Foundry and Machine Co., Buffalo, N. Y., vacuum tray dryer.
- (2E) Deming Co., Salem, Ohio, 20-hp. deep-well turbine pump.
- (3E) Denver Equipment Co., Denver, Colo., 10-hp. vertical sand pump.
- (4E) Fletcher Works, Philadelphia, Pa., suspended basket centrifuge, 40 × 24 inches, 1150-r.p.m., 730 × gravity.
- (5E) Hough, Frank G., Co., Libertyville, Ill., Payloader, Model HA.
- (6E) North American Mfg. Co., Cleveland, Ohio, Dual-Fuel burner with blower.
- (7E) Oliver-United Filters, Inc., New York, N. Y., Oliver vacuum drum filter, 8 × 10 feet.
- (8E) Shriver, T., Co., Harrison, N. J., filter presses, with wooden plates and frames.
- (9E) Sparkler Mfg. Co., Mundelein, Ill., horizontal leaf filter, Model 18-D-6.
- (10E) Universal Engineering Corp., Cedar Rapids, Iowa, jaw crusher with 15-hp. motor.
- (11E) Williams Patent Crusher & Pulverizer Co., St. Louis, Mo., roller mill with air separation.



Calcium Cyanamide

Calcium Carbide Furnace at American Cyanamid's Niagara Falls Calcium Cyanamide Plant

The three electrodes extend to same depth in furnace charge; differences in relative height are caused by staggered replacement schedule which eliminates necessity of replacing two electrodes at once

M. L. KASTENS

Associate Editor

in collaboration with

W. G. MCBURNEY

North American Cyanamid Co., Ltd., Ontario, Canada

CALCIUM cyanamide is one of the oldest large volume commercial chemicals. It was one of the first sources of artificially fixed nitrogen dating back to the last years of the nineteenth century. It has had a rocky commercial career but in spite of repeated apparent setbacks has continued to show a remarkable vitality. Its latest renaissance has been the result of new syntheses based on calcium cyanamide. The brightest spot in its future seems to be application as a chemical raw material.

Calcium cyanamide was discovered accidentally in a search for a new source of cyanide for recovery of precious metals. It did not prove to be an economic source of critically short cyanide at that time. However, just before it was tossed into the discard it was discovered that the material could be used as a direct fertilizer because of its spontaneous hydrolysis to ammonia in the ground. This hydrolysis also put it into the running as a source of ammonia gas for the production of fertilizer salts. Partial hydrolysis yields urea and this process was utilized to supplement supplies of this material during World War I. The introduction of Haber process ammonia after the end of the war placed calcium cyanamide at an economic disadvantage as a source of ammonia and urea, and it rapidly lost ground in these

markets. However, its market as a direct application fertilizer continued and even expanded during the twenties. In the middle thirties it began to pick up additional volume as its properties as a seed-bed sterilizer and defoliant were realized.

By the end of the 1930's melamine resins made from the trimer of cyanamide and formaldehyde were introduced to give the old work horse a new lease on life. These resins have enjoyed increasing acceptance and now consume in their manufacture more than half of all the North American calcium cyanamide production going into nonagricultural markets.

During the last 10 years other chemical uses have been created to compete with melamine for calcium cyanamide supply. The sulfa drugs, sulfaguanidine, sulfathiazole, sulfadiazine, sulfamerazine, and sulfamethazine have been derived from calcium cyanamide. During World War II and again during the present emergency nitroguanidine has been an important smokeless propellant. Even folic acid has been derived from calcium cyanamide commercially. The most promising new market for calcium cyanamide in terms of potential mass markets is acrylonitrile which is made from calcium cyanamide by way of calcium cyanide. The promise of this material in the production of syn-

thetic wool-like fibers is well known. Calcium cyanide itself and the sodium cyanide derived from it have become important items in the sales book.

Thus, there seems reason to believe that the production of calcium cyanamide in North America will continue the steady rate of expansion that has brought it from an initial 5000 tons per year to its present more than 200,000 tons per year.

HISTORY OF CALCIUM CYANAMIDE PROCESS

Frank and Caro (6, 7) were searching for a cyanide synthesis for Dynamit, A.-G. (formerly Alfred Nobel), when they discovered that barium or calcium carbide would absorb nitrogen when heated. Their first patent issued in 1895 (6) was devoted to the production of barium cyanide from barium carbide and nitrogen at 700° to 800° C. They merely mentioned in passing that the calcium carbide would not produce any cyanide but only cyanamides. It was not until 1898 that they patented the calcium cyanamide-from-calcium carbide process (7). In that year Cyanid-Gesellschaft went into production at Frankfort, Germany, under the Frank and Caro patents making barium cyanide exclusively. However, as the Boer War waned in 1901 the price of cyanide began to drop and at the same time Frank and Caro discovered that calcium cyanamide had value as a fertilizer (2, 3). The Cyanid-Gesellschaft reorganized, suspended production of cyanides, and built a small calcium cyanamide pilot plant at Bohneshof, Germany. On the basis of this pilot operation a 500-ton-per-year plant was built at Piano d'Orta, Italy. Both this and a smaller unit built by the Gesellschaft für Stückstoffdünger at Magdeburg, Germany, failed after a few years of operation because the externally heated retorts would not stand the higher temperature (1000° to 1600° C.) required by the calcium cyanamide process. The Magdeburg plant tried running the process at 400° to 500° C. using large quantities of calcium chloride flux but could not attain satisfactory yields (16).

In 1906 Frank discovered that if a small electrode was used to bring part of the charge up to the initiation temperature the heat released by the reaction would maintain the reaction temperature in a properly insulated oven. This discovery produced the self-heating oven with the center electrode, a modification of which is still used at Niagara Falls. The following year Frank and Caro, along with various German and Italian interests formed the Società Generale per la Cianamide, installed the new type oven in the Piano d'Orta plant, and increased its capacity to 4000 tons of calcium cyanamide per year.

With the new ovens the process proved a success. So much so that the following year when Frank S. Washburn visited Europe to obtain the American rights to the Birkeland-Eyde arc process for the fixation of atmospheric nitrogen he came back with the rights to the calcium cyanamide process instead.

American Cyanamid Operations

The American Cyanamid Co. was incorporated in July of 1907 to exploit these rights in a plant to be built at Muscle Shoals, Ala. Both technical and political difficulties led them to abandon their plans for a plant on the Tennessee River and they procured a site on the Canadian side of the Niagara River instead. The first production from this plant was obtained late in 1909. Initial capacity was 5000 tons per year.

During the first few years of operation almost all handling and sizing operations were accomplished by human strength. Lime and coke were sized for the furnaces with sledge hammers. The carbide pigs and the calcium cyanamide ingots were broken up by hand. Although there have been many refinements made in the basic process since that time, much of the present improved efficiency of the plant may be attributed to constant improvement in handling and preparation technology. These improvements together with advances in furnace design have reduced the over-

all power required to fix a ton of nitrogen from the initial 20,000 to about 9000 kw.-hr. Limestone requirements per ton of nitrogen fixed have dropped from 7.5 to 4.8 tons, and coke consumption has decreased from 3 to 1.8 tons.

The Niagara Falls plant has been expanded regularly during its 40-year life to its present capacity of about 235,000 tons per year. This rate of expansion, interrupted only during the depression years, has enabled it to satisfy the entire North American market for calcium cyanamide. During World War I a calcium cyanamide process plant was built for the Government by a subsidiary of American Cyanamid, ironically enough at Muscle Shoals, Cyanamid's first choice for a plant site. However, the plant was completed just as the war ended and it never operated after its break-in runs. It was designed to carry the process directly to the production of 110,000 tons of ammonium nitrate per year. However, the introduction of gas-synthesis ammonia processes from Germany after the war placed it at an insuperable economic disadvantage, and its total production was only 2000 tons (12).

CHEMISTRY OF CALCIUM CYANAMIDE

Commercially, calcium cyanamide is prepared in two steps. The first is the synthesis of calcium carbon from lime and coke after the equation:



This reaction is accomplished by an electric furnace process using a smothered electric arc to provide the necessary heat to melt the lime and cause it to react with the coke.

The second step in the process, which is the actual calcium cyanamide synthesis, is exothermic and requires external heating only to raise a portion of the charge to the initiation temperature which was stated by Frank and Caro (6) to be 900° to 1000° C. Subsequent studies have tended to confirm this temperature (4). The over-all reaction is



Unpublished studies at American Cyanamid laboratories indicate that this reaction produces 68.5 kg.-cal. per formula weight at 1100° C. (70.5 kg.-cal. at 0° C.). Published studies place the figure at 72 kg.-cal. (4, 11), 72.7 kg.-cal (9), and 84 to 86 kg.-cal. (8). Unpublished results at the U. S. Bureau of Standards show it to be 69.0 kg.-cal. It is believed that the reaction actually takes place in two steps. The intermediate formed has been variously given as $Ca(CN)_2$ (19), CaC_2N_2 (20), CaC (5), and Ca_3N_2 (15).

Various catalysts or fluxes are used to increase the rate of reaction or cause it to proceed at lower temperatures. The most popular seem to be calcium chloride and calcium fluoride. North American Cyanamid uses the latter. The exact function of these added materials is not completely known, but it is possible that they provide a liquid phase in which the reaction can occur. The product that is removed from the reaction ovens is in the form of a well sintered pig so that a liquid phase must be present at some point in the reaction.

Commercial calcium carbide does not melt below 2100° C., which is probably well above even local temperatures in the reaction chamber, although one investigator (19) has reported that in an atmosphere of nitrogen it will sinter at 950° and melt at 1150° C. Calcium cyanamide sublimates at about 1200° C. Calcium fluoride melts at 1360° and although the over-all temperature of the oven seldom rises above 1200° C. it is possible that local temperatures may rise that high.

Reaction rate studies have shown further that the presence of calcium fluoride reduces the temperature of optimum reactivity and increases the velocity of the reaction by 4.5 times at 1000° C.

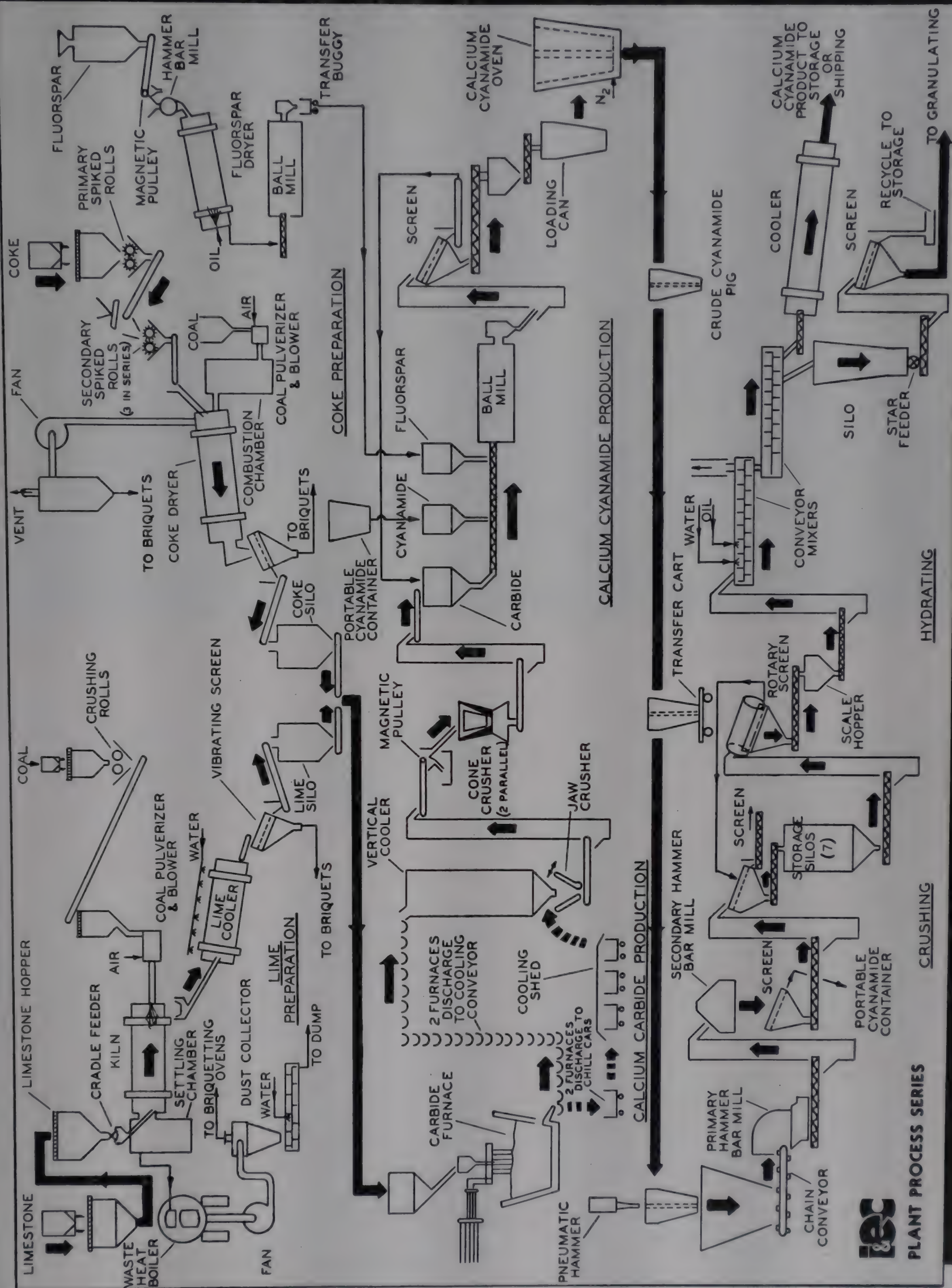


Figure 1. Flow Sheet for Production of Calcium Cyanamide at Niagara Falls, Ontario, Plant of North American Cyanamid Co., Ltd.



Briquetting Machine Where Lime and Coke Are Prepared for Use in Carbide Furnaces

(4). It has also been suggested (11, 20) that it reduces the dissociation pressure of the product calcium cyanamide.

Some mechanism other than simple melting point depression must occur since the increases in reaction rate produced by various catalysts is not proportional to their melting point depressing effects. Moissan reported (14) that pure nitrogen and pure carbide would not react at 1200°C . However, no one has been able to repeat his preparation of "pure" calcium carbide.

None of the postulated mechanisms account for the 1000°C . initiation temperature. However, the commercially important fact is that the reaction does proceed. The rate of reaction is determined primarily by the rate of diffusion of the nitrogen through the oven charge. To prevent plugging of the charge some sort of diluent is usually used along with the calcium carbide and the fluorspar. The Niagara Falls works uses recycled calcium cyanamide because it does not contaminate the finished product (17). The Russians report that they have used sawdust for this purpose (16).

NIAGARA FALLS, ONTARIO, PLANT OF NORTH AMERICAN CYANAMID CO., LTD.

All raw materials for the Niagara Falls plant are received by rail, usually in hopper cars. Outdoor stockpiles are maintained adjacent to the plant to afford a backlog of about 5 months' normal production. For most operations rail shipments are unloaded

directly into the feed preparation plant upon receipt. No attempt is made to rotate the stockpiles. However, when it is necessary to draw upon this reserve, a clamshell crane loads the material from the stockpile into regular railroad hopper cars which are then unloaded at the preparation plant in the usual manner.

Coke

Carbon for the carbide reaction at Niagara Falls is obtained from various sources. Most of it is obtained as metallurgical grade coke although a high degree of mechanical strength is not essential. At present the coke supply comes from vertical retorts or beehive ovens. However, there is apparently no reason why coke made in other types of ovens, which can process expanding coals not suitable for metallurgical coke, could not be used if it were available. Some work has also been done which indicates that so-called low temperature char could be used. Charcoal has been used, but its low density makes it unsuitable for furnace charging. Actually any sort of carbonized material having a low ash content and low electrical conductivity (13) is suitable. As coking grade coals become increasingly scarce, it is probable that some substitutes will be used.

Carbonaceous materials other than coke are presently added to the charge of the carbide furnaces. The addition of petroleum coke reduces the conductivity and ash content of the reaction bed. The use of petroleum coke is limited almost entirely by its availability. Percentages up to 40% have been used; however, Cyanamid currently adds something less than 10%, depending upon the supply situation. Raw anthracite coal may also be used in the charge since it has a high carbon content and relatively low conductivity. The Niagara Falls plant sometimes uses as much as 10% of this material in the carbon charge, again depending on its availability.

TABLE I. MATERIALS REQUIREMENTS PER TON OF NITROGEN FIXED

Limestone, tons	4.8
Coke, tons	1.86
Coal, tons	1.0
Power, kw.-hr.	9000
Labor, man-hr.	13.5

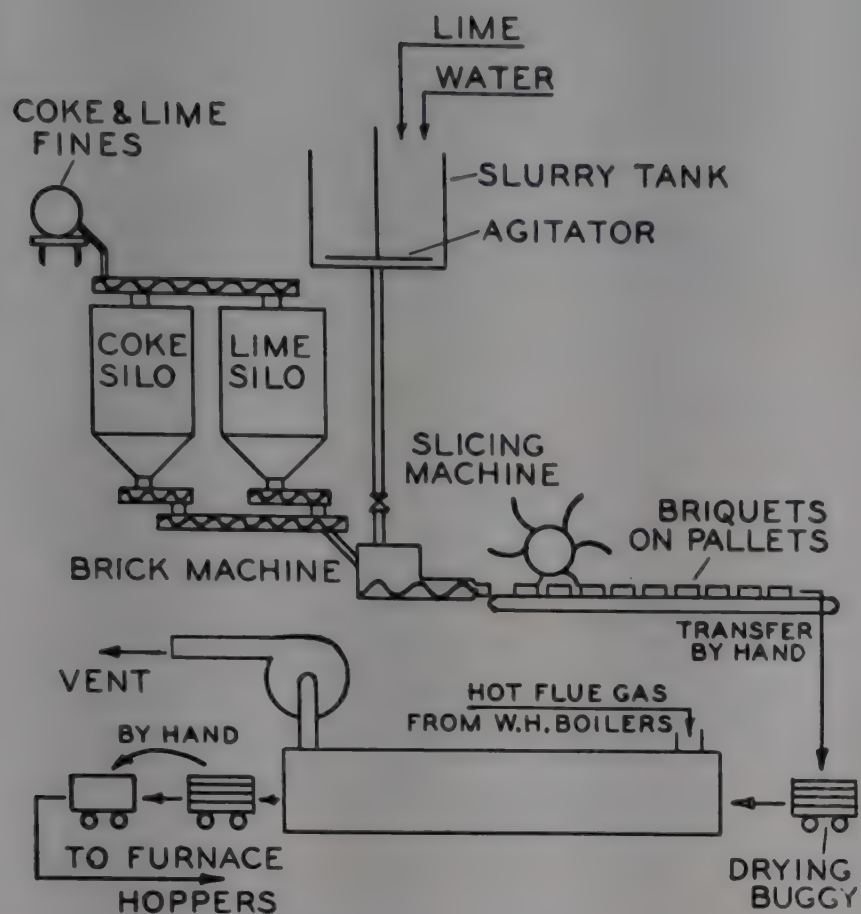


Figure 2. Briquet Production

Coke, as it is dropped from the hopper cars, passes between toothed rolls with a clearance of $2\frac{1}{2}$ inches between the rolls. Rubber belt conveyors then carry it through a series of three similar mills which reduce the particle size to an ultimate maximum of 1 inch (2E). After leaving the fourth mill the coal is screened (22E), and the material over 1 inch is recycled to the feed of the No. 1 mill. The properly sized material goes to two parallel rotary dryers, heated by a countercurrent stream of flue gas from a pulverized coal fired combustion chamber. The coke is discharged with a moisture content of less than 1%. The dry material is screened again (20E) and conveyed to one of nine 40-ton storage hoppers. These are the first holding hoppers in the coke preparation mill. All coke must either be processed directly from the railroad cars to this point or stored on outside piles as it is received.

Lime

Lime for the carbide furnaces is produced at Niagara Falls by burning limestone from the Cyanamid quarries at Beachville, Ontario, 100 miles from Niagara Falls. The material is quality-controlled at the quarries and crushed to size there. Both 2-inch and 1-inch limestone are received at the plant. These two size grades are blended, after burning, using 60% of the larger size.

As the limestone is received in the pits below the unloading tracks it is conveyed to seven 240-ton hoppers. From these hoppers a belt conveyor feeds seven rotary kilns, each with a capacity of 100 tons of lime per 24-hour day. The kilns are heated directly by the combustion of about 50 pounds of pulverized coal per minute. The Niagara Falls kilns are 125 feet long. Practice in recent years has tended toward longer lime kilns—up to 300 feet. These longer kilns improve the heat efficiency of the operation as much as 50%, requiring perhaps 6,000,000 B.t.u. to burn a ton of lime as compared with 9,000,000 B.t.u. required by the Niagara Falls kilns. However, exhaust gas from the kilns at Niagara Falls is passed through waste heat boilers which reduce its temperature from 1100° to 450° F. The discharge from the boilers along with some uncooled gas is then used in the tunnel dryers in the briquetting department. Another portion of the off-gases is used in spray-drying operations in another department. These procedures result in heat efficiencies comparable to those which would be obtained from longer kilns.

The discharge from all of the kilns falls into a single bucket conveyor (13E) which carries the burnt lime into a rotary cooler. This cooler was constructed by Cyanamid engineers of two concentric cylinders with an annulus of 12 inches. Six longitudinal plates support the central cylinder and divide the annulus into six separate compartments to reduce breakage of the lime. Water running over the outside cylinder and air passing through the center reduces the temperature of the lime from 1000° to 300° F. A steel apron conveyor receives the cooled material and carries it to a screen with 0.090-inch openings (23E). The material that passes through the screen is conveyed to the briquetting department, the oversized material going to storage hoppers with a combined capacity of 800 tons. About 2 to 5% of unburned calcium carbonate is left in the kiln product to produce optimum efficiency in the carbide furnaces (10).

Fluorspar

The fluorspar used as a flux in the calcium cyanamide reaction is about 93% pure calcium fluoride and comes largely from Newfoundland, although on occasions the material has been obtained from Mexico. It arrives at the Niagara Falls plant in hopper railroad cars in the form of large chunks averaging 4 to 6 inches in diameter. It is first reduced in a hammer bar mill (11E) which brings its size down to about $\frac{1}{4}$ inch. It is then dried in an oil-fired rotary dryer, which reduces the moisture content to less than 0.1%. The fluorspar discharged from the dryer is transferred by a screw conveyor to a ball mill which further reduces its size. The discharge from the ball mill is received by transfer buggies, having a bottom discharge, which carry the material to a vibrating 20-mesh screen. The oversize from this screening is returned to the ball mill, and the undersize is received by a screw conveyor which carries it directly to the oven feed hoppers. Fluorspar is ground only as needed by the oven room.

Briquetting

Very fine particles of lime or coke cannot be charged to the carbide furnaces because they tend to clog the charge and may result in explosive release of product gases. They may also reduce resistance of the bed and cause the electrodes to ride up out of the charge and result in very inefficient operation. However, about 10% of fine material (under 0.1 inch) is produced in the coke milling and the screening of the burnt lime produces about 7 tons of dust per kiln per day. This material is collected from the screens collectors for reclaiming; it is combined in the proportions of 2 parts of carbon to 3 parts of lime and made into a paste by the addition of about 10% of lime slurry. The paste is extruded as a slab, 2×8 inches, onto a belt conveyor. As it travels along the belt it is separated into 2- to 3-foot lengths and scored with knives into 2×3 inch rectangles. The scored slabs on sheet-metal trays are placed in rolling racks, holding about 50 slabs, and rolled into one of three tunnel dryers. Lime kiln exhaust gases which have passed through a dust collector provide the heat for the dryers. The temperature of the dryer is held at 350° to 400° F. by adjusting the proportion of gas taken directly from the kilns to that taken from the waste heat boiler. The briquets pass through the dryer in about 8 hours, are dumped into transfer cars, and taken to the furnace feed conveyor belt where they will be introduced into the furnace charge.

Calcium Carbide Production

Weigh hoppers (10E) beneath the coke and the limestone storage bins discharge to converging belt conveyors which mix the lime-coke charge in transit to the carbide furnaces. Proportions are controlled by adjusting the speed of the belts to maintain 10 to 15% excess of lime over stoichiometric proportions of 56 parts of lime to 36 parts of coke. The exact proportions are not critical, and experienced operators can control the mix by visual observation. From the mixing belt the charge is picked up by

bucket elevators which carry it to feed hoppers located above the carbide furnaces.

Furnaces. Furnaces of various sizes have been used at Niagara Falls and some of the smaller ones are still occasionally pressed into service in emergencies. However, primary production is maintained by a battery of two 20,000-kw. furnaces and two 10,000-kw. furnaces. German plants have installed furnaces up to 30,000-kw. capacity. However, Cyanamid engineers believe that over-all efficiency drops off somewhere above 20,000-kw. Although the furnaces in this plant are essentially square, circular furnaces with the electrodes introduced in a triangular pattern and elliptical furnaces with in-line electrodes are used. Changes in design are made largely for construction considerations. These do not affect the performance of the furnace since most of the reaction takes place within 1 foot of the electrodes (10).

The Niagara Falls furnaces are essentially firebrick-lined steel boxes with a taphole about 18 inches from the bottom on one side. The firebrick floor of the furnace is covered with 3 feet of electrode carbon blocks cemented with pitch. This is the only refractory known which will stand the high temperatures of the operation combined with the high alkalinity of the molten lime. The sides of the furnaces are not subjected to such vigorous conditions since they are effectively insulated by a nonreacting mass of charge and product. Nine inches of common firebrick serve for these surfaces.

The external dimensions of the two larger furnaces are 41 × 45.5 feet at the top and 29 × 11 feet at the bottom; they are 18 feet high. The smaller ones are 21 × 27 feet at the top, tapering to 17 × 25 feet at the bottom, and 11 feet high. In a newly bricked furnace the taphole is about 6 inches in diameter. However, in use the carbon blocks surrounding the taphole gradually burn away. The lip of the taphole is a water-cooled casting.

ELECTRODES. Each furnace is equipped with three composite electrodes. Each electrode in the larger furnaces consists of five 20 × 22 inch rectangular electrolytic-carbon rods which are held in a line to give a composite cross section of 20 × 110 inches. The electrodes in the smaller furnaces are constructed of four of these components, similarly arranged. The rods are attached to the water-cooled, cast-bronze header by means of two horizontal water-cooled bolts. The components are constructed with a threaded cavity 8 inches in diameter and 10 inches deep at the top and bottom. In making up a new electrode a graphite threaded plug is inserted for half its length into the tapped hole in the bottom of the new rod. The remainder of the plug is then screwed into the hole in the top of a stub removed from the burned out electrode. In this manner the electrodes can be used completely.

However, it is essential that there be no air space between the plug and the rod or the electrode will overheat and break off. The possibility is avoided by very careful machining of both the plug and the tap.

Paste cannot be depended on to complete the contact in the threaded section although it is sometimes used between the abutted ends of the carbon rods. The upper half of a new electrode assembly is protected by a thin layer of ordinary cement held in place by 1-inch chicken wire. This prevents oxidation or burning of the portion of the electrode which is not initially submerged in the furnace charge.

Both the water and the electrical connections to the electrodes are flexible to permit the vertical adjustment of the electrodes. An automatic mechanism operating a cable drum over the furnace adjusts the height of the electrodes to maintain a constant resistance through the reaction bed. Under normal conditions 1 to 3 feet of the electrodes are buried in the charge. If the resistance in the bed increases the electrodes are lowered so as to present more surface to the reactants. If the resistance of the bed is reduced, usually because of an excess of carbon in the charge, the electrodes will rise and if there is too great an excess of carbon they will "ride out" of the bed completely. When this condition appears imminent additional lime is shoveled directly onto the top of the bed around the electrodes. As the bed settles, the lime increases the resistance around the electrodes and allows the electrodes to drop back into normal position. This condition is somewhat chronic, and it is usually necessary to add lime to the electrode area regularly throughout the melt.

The electrodes in the furnace are gradually burned off at the bottom and must be replaced after about 170 hours of operation.

When such replacement is necessary the electrode assembly is lifted out of the furnace, disconnected from the cooling water and power lines, and replaced by a new assembly.

Although the entire electrode assembly weighs about 16 tons permanent cranes and quick-acting connections enable two workmen to change an electrode in less than 20 minutes. When new electrodes are introduced into the furnace they are slowly lowered under manual control, with the power on, until they strike an arc through the reactant bed; this avoids the power surge which would occur if the electrodes were allowed to come into the bed by means of the automatic control.

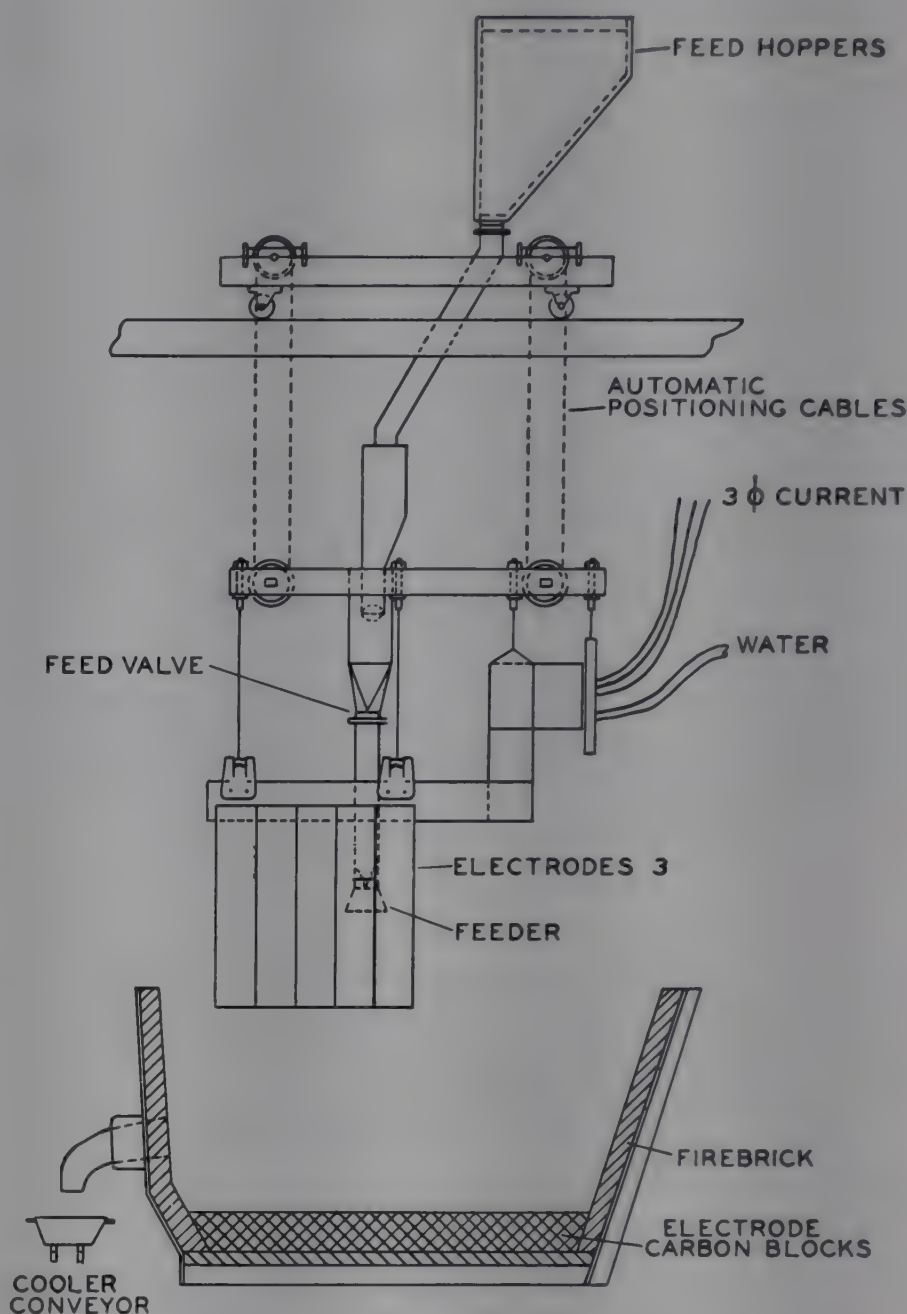


Figure 3. Carbide Furnace

Another electrode system is used at the TVA plant in which sliding contacts replace the header used at Niagara Falls. This arrangement permits the addition of electrode components without removing the assembly from the furnace.

Componental electrodes are gradually being replaced throughout the carbide industry with continuous electrodes of the Söderberg type, and Cyanamid plans to eventually make the change in their works. In the Söderberg electrode a paste of buckwheat-sized carbonized anthracite, coke fines, and tar is packed into the top of a 40-foot, thin steel tube. The entire tube serves as an electrode and is fed into the furnace as it burns away from the bottom. As the paste moves closer to the surface of the charge it is slowly baked so that when it has reached the 6-foot section below the sliding electrical contacts it has great mechanical strength. As the electrode is consumed additional tubing is welded to the top and filled with the carbon paste. Suspension is by means of steel straps progressively welded to the sides of the tube and reeled out as required to feed new electrode into the furnace. The entire assembly is raised and lowered by an automatic mechanism similar to that used with componental electrodes to maintain constant amperage in the furnace.

GAS COLLECTION. At the North American Cyanamid plant four water-cooled refractory hoods extend over the bed of the furnace between and alongside of the electrodes. These hoods are

connected to a common collector outlet which leads to a scrubber (4E). Water sprays playing on a high speed propeller fan in the scrubber ensure that solid particles entrained in the gas stream are wetted and carried off with the water. The fan is designed so that it provides almost no suction at the hoods since suction at this point would act as a forced draft on the furnace and burn up some of the coke before it could react. The gas discharged from the scrubber is mostly carbon monoxide and hydrogen and is fed into the lime kilns to augment the coal flame. Only a trace of oxygen and carbon dioxide is present.

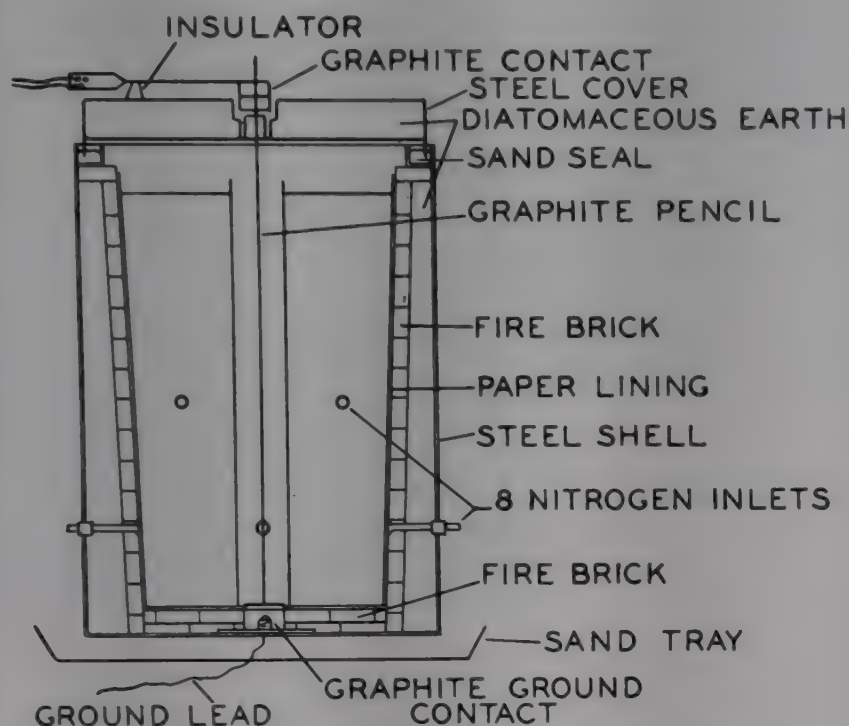


Figure 4. Self-Heating Oven

The gas collection system handles about 1000 cubic feet of gas per minute from each of the large furnaces; this represents almost all the off-gases. The small amount that leaks around the hoods escapes through roof vents over the furnaces.

In recent years many closed carbide furnaces have been built, mostly of the circular design mentioned. This design eliminates the need for gas-collecting devices but does not appear to enhance the heat efficiency of the installation appreciably, since a negligible percentage of the energy applied to the system is lost as radiant heat.

FURNACE OPERATION. The lime and coke charged to the furnace is introduced from the feed hoppers by long tubes, 8 inches in internal diameter, which hang between the electrodes and alongside the outside electrode. The center feeders have roof-shaped deflectors and the outer ones single-pitch deflectors, which throw the charge against the side of the electrodes. Curved slide valves between the feeders and the feed hoppers are closed when the feed pipe is vertical and open when it is moved forward or back. When the operator wants to charge to the furnace he hooks a long rod onto the end of the feeder tube and pushes it back and forth, thus opening the valve and distributing the charge along the electrodes at the same time. The furnace charge must be augmented in this fashion every 5 to 10 minutes.

As the furnace continues in operation fused solid impurities in the charge gradually build up a layer on the furnace floor. Once this layer rises above the level of the taphole it is usually necessary to shut down the furnace and clean it out. A hump of solid calcium carbide also often forms at the back of the furnace opposite the taphole. This hump tends to grow slowly until it obstructs the flow of the molten product from the taphole. When either of these conditions necessitate a shutdown the electrodes are lifted from the furnace and charge is allowed to cool from 4 to 7 days. The cooled charge is almost a solid mass which must be

broken up with air hammers and removed by crane bucket. Since it is impractical to wait until the entire mass has cooled the hammer operators wear heavy wooden clogs and work down into the furnace as fast as the temperature permits. Fortunately, this operation is only necessary about every 3 years.

Flow through the taphole is maintained by ramming the charge with 1-inch steel rods about 15 feet long. The rods can be inserted in the bed for about 30 seconds before they become so flexible that they are ineffective. However, the rods can be removed, cooled in the air, and then re-used. If the flow becomes excessively sluggish the taphole is "needled"; the needle is a graphite electrode 4 inches in diameter and 4 feet long connected to one phase of the power source and suspended from an overhead running hanger. When it is inserted in the taphole it strikes an arc through the charge to the main electrodes and raises the temperature in the vicinity of the taphole. When it is desired to shut off the flow from the taphole, the operator merely shovels about a bushel of cold carbide into the opening. This treatment produces sufficient local cooling to stop the flow of molten carbide. To reinstitute the flow the taphole is opened by use of the "needle."

A potential of about 200 volts and as much as 70,000 amperes across the electrodes produces a temperature of 2000° to 2200° C. (10) in the molten charge of the furnace, although in the actual heating arc much higher temperatures are attained. Under these conditions the furnace product contains about 90% calcium carbide although 95% pure product can be made under ideal conditions. The two large furnaces discharge continuously at a rate of about 6 tons per hour into a bucket conveyor. This conveyor doubles back on itself to provide air cooling for the carbide. Preliminary cooling reduces the temperature from 4000° to 300° F.

The smaller furnaces follow an older procedure whereby the charge is tapped intermittently into cooling cars which hold approximately 2000 pounds. These cars are about 2½ feet wide by 4 feet long by 3 feet high, constructed of 2-inch plates of cast steel. When the product is handled in this manner cooling must be accomplished by storing the cars in an open-sided shed for about 24 hours.

Carbide Milling. Carbide from the cooling hopper or from a conveyor running from a pit into which the chill cars are dumped is fed into a jaw crusher with a jaw clearance of 6 inches (3E). A bucket conveyor distributes the jaw crusher discharge between two cone crushers (14E) which further reduce the size of the carbide to a maximum of 1 inch. The 1-inch carbide is collected in a feed hopper. This hopper, together with similar bins for fluor-spar and recycled +6-mesh calcium cyanamide, feed through variable-speed screw conveyors to a ball mill which ensures an intimate mixture of the components while pulverizing them to -100 mesh. The mill is divided into three chambers having progressively smaller steel balls.

Because atmospheric moisture will react with the carbide to form explosive acetylene, the carbide mills and the conveyors are blanketed with nitrogen to exclude both moisture and oxygen. This nitrogen is supplied at ½ inch of water pressure from the liquid air machines that serve the calcium cyanamide ovens.

Calcium Cyanamide Production

The discharge of the ball mill is received by a conveyor which transfers the material to a vibrating screen (21E). Material which is screened out is returned to the mills. The fine material is conveyed by belt conveyor to a loader hopper in the calcium cyanamide oven room. The loading hopper fills loading cans which are placed on a scale underneath the hopper discharge. The loading cans are made of ½-inch steel plate in the shape of inverted truncated cones. These cans discharge from the bottom and serve the purpose of oversize funnels.

Self-Heating Oven. At the present time most of North America's production of calcium cyanamide is achieved in a



A carbide charge is transferred in a loading can and dropped into an open oven; this is start of final step in cyanamide production



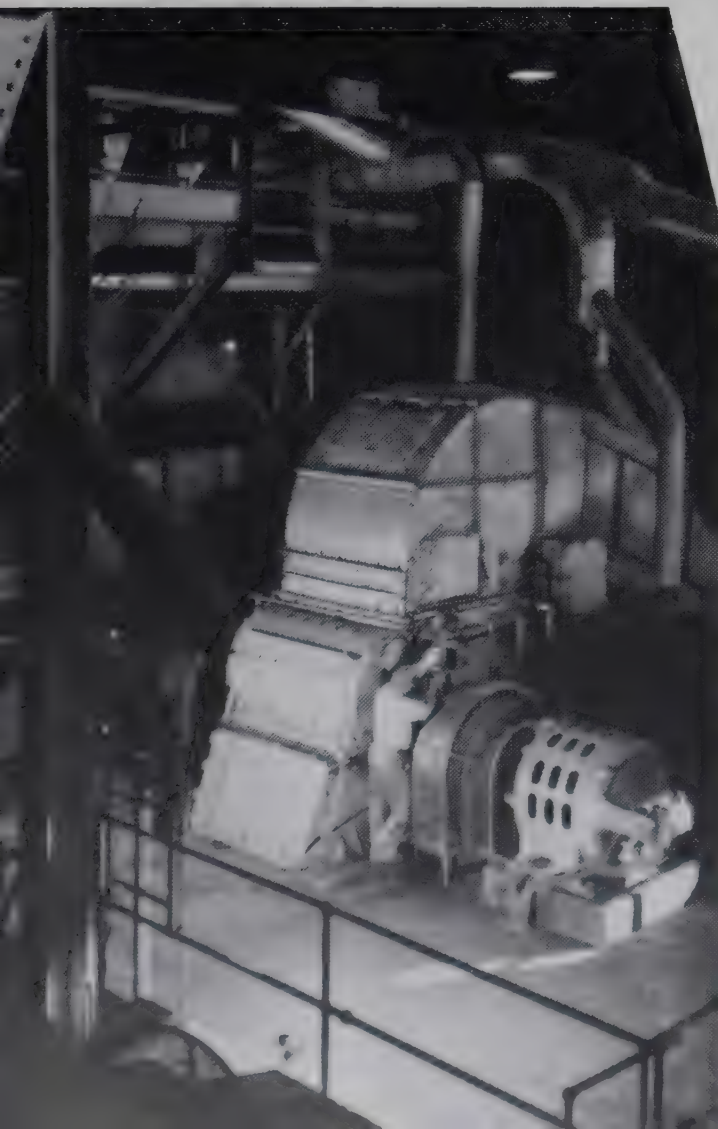
In oven rooms, after 7.5 days of nitrification, solid pigs are removed from ovens and allowed to cool (background) for about 8 days



A pneumatic hammer is dropped into the center cavity of cooled pig and cracks it into pieces which can be fed to the primary crusher

CALCIUM CYANAMIDE PRODUCTION

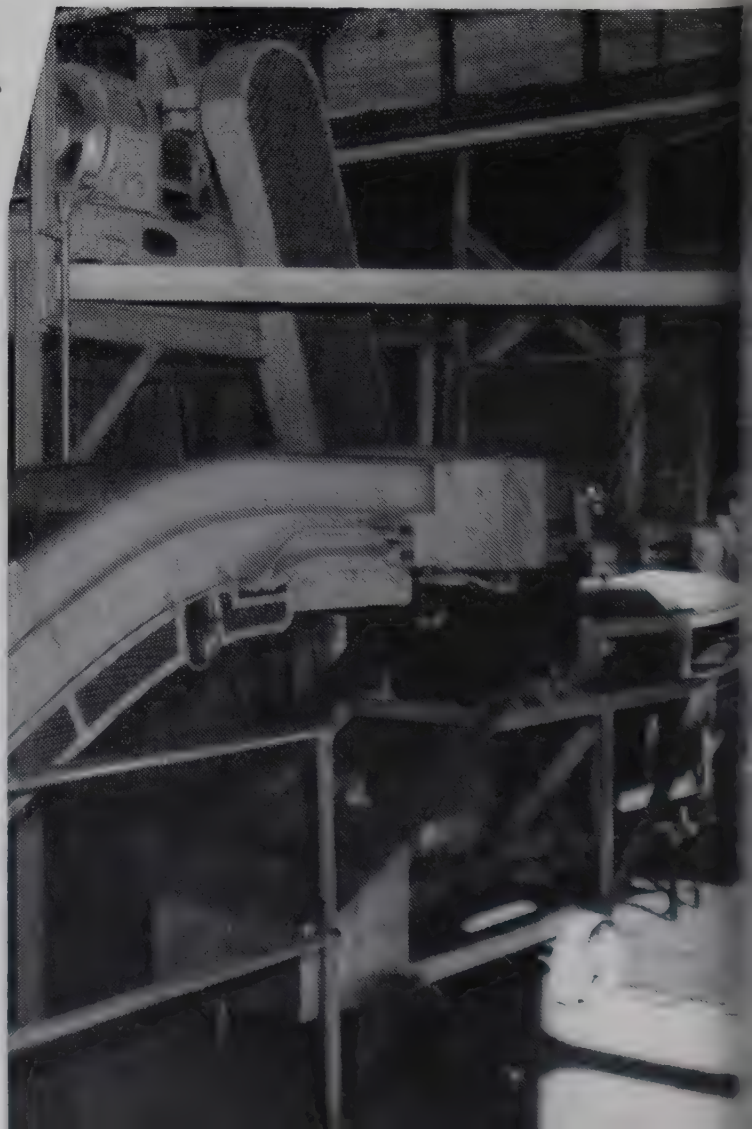
After primary crushing operation, large bar mills pulverize the lumps of crude calcium cyanamide



This rotary tumbler forms granules from calcium cyanamide fines, which are cooled and then bagged for fertilizer



Portable conveyors take the 100-pound bags of granular product directly into box cars for shipment



battery of 4-ton ovens. The original ovens at Niagara Falls had a capacity of 700 pounds (12) and 2- and 3-ton ovens have been constructed in the past. The smaller units seem to have no advantage over the 4-ton size and require a greater expenditure of labor per ton. Five-ton and even some 10-ton ovens are used in Europe and have been used at Niagara Falls, but Cyanamid operators find that they offer no advantages over the 4-ton size since they usually require several starting electrodes and are very slow to cool. The ovens are vertical and have the shape of a slightly tapered cylinder with the large end at the top. They are lined with an ordinary firebrick which is specially formed. The oven is jacketed with $\frac{1}{2}$ -inch steel and insulated with 6 inches of diatomaceous earth held in place by a thin sheet-iron shell. The entire assembly rests on a sand mat. The ovens are arranged in the oven room so that the outer rims nearly touch with access walks provided between every second rank.

To prepare the oven for charging, a large steel tube capped at the top is fitted into the center of the oven. A gantry positions the filled loading can above the open oven, and the oven operator trips the bottom discharge allowing the 4-ton charge (± 10 pounds) to drop into the oven. The center tube is lifted from the oven by the gantry crane and placed in the next oven along the line leaving a central cavity through which nitrogen can circulate. The crane then picks up the cover and swings it into place on top of the oven. The edges of the cover are sealed in a sand trough.

The loaders begin at one end of the oven room and prepare one oven after another for the charge. They work continuously through the oven room and at the end of the $7\frac{1}{2}$ -day soaking period they are ready to begin again. An unloading crew works about $\frac{1}{2}$ day ahead of them, unloading the ovens in the sequence in which they were charged.

OVEN REACTION. Nitrogen at about $\frac{1}{2}$ inch of water pressure is introduced into the oven through inlets, located on two levels along the side of the oven. Since the charge does not come up to the top of the oven cavity, the nitrogen diffuses between the paper liner and the firebrick, gradually works its way to the top of the oven, and then down the center cavity. About 60% of the nitrogen introduced actually goes into the nitrification reaction. The remainder is used for flushing the system and for cooling the fully reacted pig. The reaction begins at the center of the pig and gradually works toward the outside. During the latter stages of the oven cycle the reaction will begin along the outer perimeter of the pig and work in toward the center. It has been reported (18) that lime kiln exhaust gases, scrubbed to reduce their carbon dioxide content to 0.5 to 1.0% can be used in place of pure nitrogen for the calcium cyanamide reaction, but this technique has never been explored commercially.

To begin the oven reaction a graphite pencil is inserted through a small hole in the center of the oven cover. This electrode reaches all the way to the bottom of the oven where it rests on a bottom contact. A current passed through the electrode for 1 to $1\frac{1}{2}$ hours raises the temperature of the surface of the inner cavity to the initiation temperature of the reaction (about 1000°C). Once initiated the exothermic calcium cyanamide reaction is self-sustaining. The oven insulation is designed to maintain a temperature of about 1100°C in the charge to attain maximum nitrification (4).

After about 6 days the nitrification is normally completed. Allowing 1 day for cooling, the ovens are opened on the seventh day by the unloading crew. Specially designed tongs dropped into the central cavity by the gantry crane grip the pig from the inside so that it may be lifted up and transferred to a cooling room, adjacent to the oven room.

Occasionally the pigs will crack during the reaction or be broken in the attempt to lift them from the oven. In such cases it is necessary for special crews to drill diagonal holes into the segments of the pig with air hammers. Steel rods are driven into these holes and lashed together with chains to provide a new purchase for the crane.

The Cyanamid pigs have a black appearance except for the white rosettelike patterns around the nitrogen inlets which are caused by calcium oxide, formed by the small oxygen impurities in the nitrogen stream. Actually calcium cyanamide is white. The black appearance of the pigs is due to the presence of 12% of free graphite carbon formed in the reaction. The remainder of the pig is composed of about 70% calcium cyanamide, 12% free lime, and $\frac{1}{2}$ % unreacted carbide.

Many attempts have been made to devise a continuous process for the production of calcium cyanamide. Tunnel-type furnaces with countercurrent flow of nitrogen and carbide have been constructed but their low (approximately 85% of theoretical) yields did not justify their high initial cost (1, 4). Rotary furnaces have been more successful. One at Knapsack, Germany, using a temperature gradient of 780° to 1000°C and a residence time of 24 hours claims to give efficient production of high purity product containing 22 to 23% nitrogen (4, 11). However, the occurrence of lumps from the plastic phase of the reaction is believed to result in high residual carbide content in the product.

Calcium Cyanamide Milling

The pigs from the ovens at Niagara Falls are allowed to stand in the cooling room for about 8 hours; this brings their exterior temperature down to about 75°F . They are then picked up by an outside jacket grip and transferred to a breaking stand built of steel girders. An air hammer dropped from a permanent crane into the central cavity breaks the pig into several large pieces which fall from the stand onto a drag conveyor below, which carries them into a heavy duty bar mill (24E). This mill reduces the pieces to about 2 inches in maximum diameter and discharges onto a belt conveyor which takes the crude product into one of two secondary bar mills (25E); here the pieces are reduced to a maximum particle size of about $\frac{1}{8}$ inch. These mills discharge to a vibrating 6-mesh screen (18E), the oversize being returned to the secondary bar mills. From this primary screening the material is carried by bucket conveyors to a series of sizing silos which separate it into +6 mesh, -6 mesh, -16 mesh, and other size categories as desired. There are nine of these silos in all, with an individual capacity of 550 tons.

Hydration. All the calcium cyanamide product undergoes varying degrees of hydration. The so-called "minimum hydrate" is intended for use as a chemical intermediate and is largely consumed at the Welland Works of North American Cyanamid. This material is drawn from the storage silos at the desired size and transmitted by screw conveyors to a $\frac{1}{2}$ -inch-opening rotary screen and then to a mixer conveyor. The conveyor has a series of pusher-paddles rotating on a central shaft. A water spray at the head of the conveyor adds enough water to react with the residual carbide. Material from the hydrating mixer is dropped into another similar mixer conveyor in which no additional water is added; it is then transferred to a rotary cooler which will absorb most of the heat produced by the hydration reaction. The cooler is merely an unlined steel cylinder and does not employ any external cooling. It discharges through a $\frac{1}{2}$ -inch screen to belt conveyors which transport the product either directly to tank cars for shipment or to storage tanks.

The next most highly hydrated product is the so-called "pulverized" grade intended for fertilizer use. Two to four per cent of oil is introduced into this material to reduce dusting, a former objection of farmer consumers. The water added in the mixer conveyors is theoretically enough to decompose any residual carbide present and, in addition, to hydrate most of the calcium oxide formed in the calcium cyanamide ovens. Actually the last small percentage of calcium oxide is very difficult to hydrate because it is not physically accessible. The pulverized cyanamide passes through the mixer conveyors and the rotary cooler, then either to tank cars for shipment or to storage.

The largest volume of the calcium cyanamide produced cur-

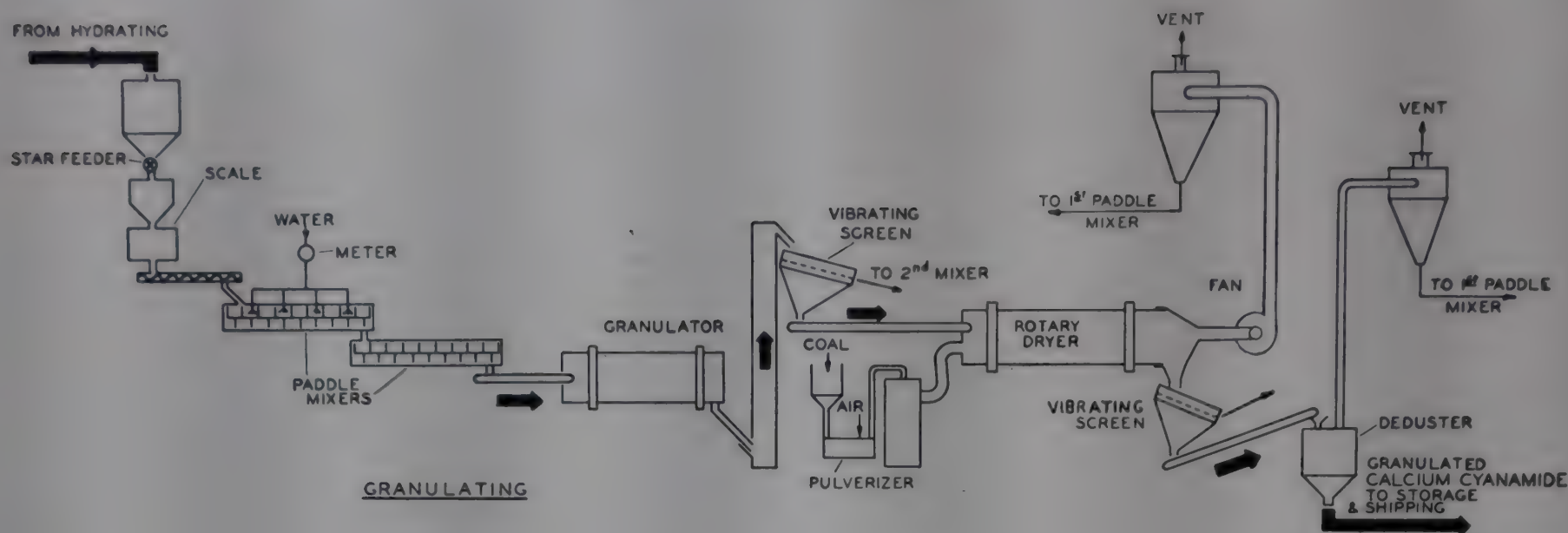


Figure 5. Flow Sheet of Granulating Operations

rently goes into the "granular" grade which is also used as a fertilizer. Water is added to this material in the mixer conveyors. After the initial hydration the product is screw conveyed to a rotary screen and then to weigh hoppers which discharge continually into a mixer-conveyor similar to that in the hydrating department. Additional water is introduced into the product in the mixer-conveyor. The material passes through another mixer-conveyor to stabilize the moisture content and then into the granulator which is just a large rotary tumbler. The discharge from the granulator drops onto a belt conveyor which takes the product to a vibrating screen (19E) which rejects the oversize material and returns it to the head of the granulator. The material passed by the screen is conveyed by a belt to a rotary dryer. The dryer discharges into a dust separator which removes the fine powder caused by abrasion of the pellets and returns it to the granulating department feed hoppers. The clean granules are conveyed by belt to storage hoppers.

The granulated material is shipped in 100-pound bags. A special bagger at Niagara Falls fills, weighs, and seals these bags automatically (5E). The bags ready for shipment usually pass over roller conveyors where suitable labels are attached by hand, past an electric eye counter, and directly into box cars for shipment.

Auxiliary Equipment

Power for the carbide furnaces at Niagara Falls is provided by three 7250-kv.-amp. single-phase 25-cycle transformers (8E); 25-cycle current is preferred because of its greater heating efficiency and ease of control. However, 60-cycle current could be used and when the new development of Niagara Falls' power is completed American Cyanamid may use some power at that frequency. When operating at full capacity the large furnaces draw 70,000 amperes of current from this power source. The current is carried through a fire wall to the contacts of the flexible connectors by a composite bus bar made up of sixteen $12 \times \frac{7}{16}$ inch copper plates spaced $\frac{7}{16}$ inch apart. There is a separate bus for each phase. The present transformers provide a single current phase to each of the three electrodes. However, three-phase transformers, now on order, will provide greater flexibility of operation.

Nitrogen, for the process, is produced in a battery of liquid air machines, located in a building adjacent to the oven room. The conventional Claude machines (12E) will produce a product which is more than 99% nitrogen. Air intakes for the compressors are located at three sides of the plant site and the actual feed is always taken from the upwind intake. If traces of acetylene were present in the intake air either the compression or acetylides formed from copper fittings in the liquefiers would certainly cause an explosion. Oxygen, produced along with the nitrogen

in the Claude machines, is piped to the company's Welland Works 8 miles away where it is used to enrich the air stream to gas reformers in the ammonia plant.

All the kilns and dryers in the plant with the exception of the fluorspar dryer, which uses oil, are heated by pulverized coal fluidized with air and burned at a combustion nozzle. In the kilns the nozzle is installed directly in the inside of the cylinder. On the dryers a cylindrical firebrick combustion chamber is provided where the fuel gases attain a temperature of 1600° to 1800° F. Natural draft carries the hot flue gases from the top of the furnace into the drying chamber. The fuel is received as $\frac{1}{4}$ - to 2-inch nut slack coal and is reduced to a maximum of $\frac{3}{4}$ inch in a roll crusher. A hammermill pulverizer (9E) further reduces it to 50% through a 200-mesh screen. Preheated air taken from ducts over the hot lime conveyors is blown through the pulverizers and carries the coal directly to the burner nozzles.

Various types of conveyors are used throughout the plant depending on the service required. For cool materials being transported over considerable distances, rubber belt conveyors are employed. For shorter movements closed screw conveyors are used. For moderately hot materials steel apron conveyors are favored, but special hinged bucket conveyors have been designed to receive the discharge of the lime kilns and the large carbide

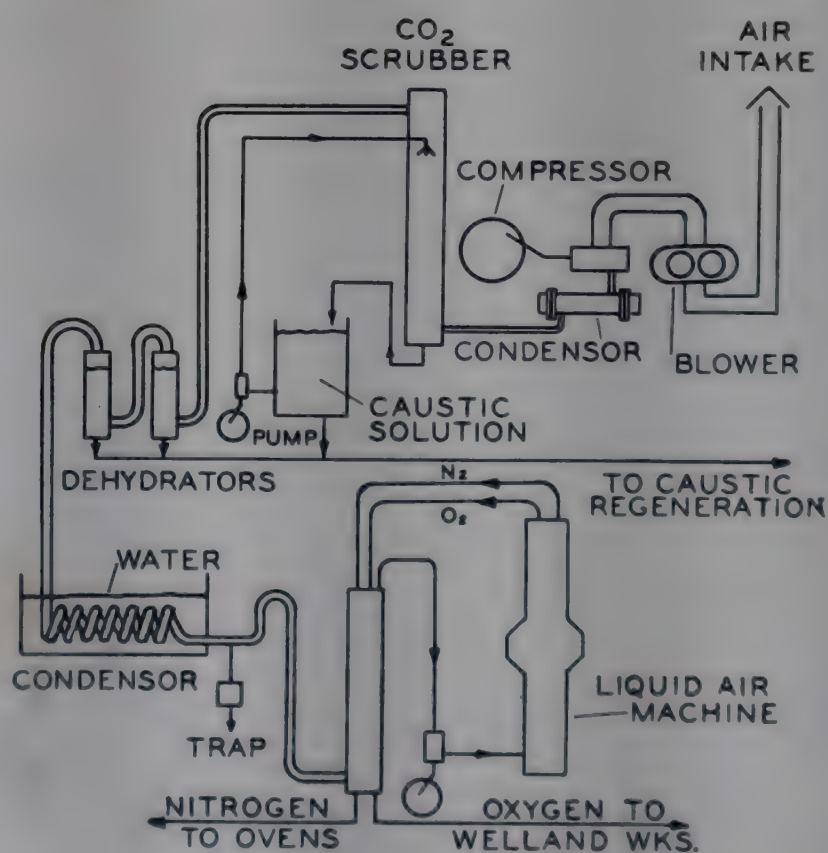


Figure 6. Liquid Air Production



Specially Designed Cooling Conveyor Moves Molten Calcium Carbide from Two Largest Furnaces

furnaces. Vertical lifts throughout the plant have been accomplished by the use of bucket hoists.

A few departures have been made from the conveyor practice described: A drag type conveyor has been installed to take the milled calcium carbide to the ball mill hopper. This installation was tried as a possible alternative to the screw conveyors used elsewhere in the plant, but it seems to offer no special advantages. The large chunks of calcium cyanamide, before they reach the first bar mill, are moved with a heavy "chain" conveyor which uses transverse bars to drag the pieces up an inclined steel plate. The large heavy pieces handled here require such equipment, but there is no comparable need in the rest of the process. In the granulating department some very fine material is fluidized with air and moved in chutes. The bottom of the chute is partitioned horizontally by a canvas diaphragm. Air introduced into this area seeps through the canvas to fluidize the powder and greatly reduce its angle of repose. This technique is a fairly recent development but seems to give very satisfactory service.

Dust control and collection is achieved primarily with conventional cyclone separators manufactured in the plant shops. However, bag filters are used in the product milling rooms (7E) and the shipping departments (1E).

Dust collected from the kiln stack gasses is slaked with water and dumped because it is too badly contaminated with fly ash and other impurities from the coal to be used in the production of carbide. The calcium carbide dust collected every day from the carbide milling operations is also slaked and discarded. Because of its small particle size it has a large relative surface area and reacts with the atmosphere too rapidly to be of practical use. If any acetylene was generated on the plant site these fines could probably be used economically for that purpose.

Chemical Control

Chemical control of the calcium cyanamide process at Niagara Falls is not so much aimed at keeping the raw materials and process steps within specifications but to detect variations that do exist so that the process conditions can be adjusted accordingly.

This situation is the inevitable result of a process based completely on natural products, the composition of which cannot be controlled.

Each shipment of coke received (about 1250 tons) is subjected to an A.S.T.M. proximate analysis, water and sulfur determination, and apparent density by water displacement. The results serve only to check the source of the coke and indicate, for future use, whether or not it is desirable raw material. The prime criteria for this process are low ash density and low conductivity. The carbon content should be above 88%. However, under present conditions, or, any foreseeable future conditions, availability weighs as heavily as suitability.

Moistures are also run on the coke once a day, or oftener if the type of coke is changed, to check the efficiency of the coke dryer. Also, as a check on the charge preparation operations a screen analysis is run on the screened, dried coke. The sizing of the furnace coke charge is held to a maximum of 2% over 1-inch and nothing through a 0.42-inch screen.

The efficiency of the lime kilns are checked daily by determining the residual calcium carbonate in the burnt lime. This figure usually runs about 2.5%. Although the Cyanamid quarries furnish analyses with each shipment of limestone the plant runs weekly calcium carbonate checks on a composite sample representing all shipments received. Informal specifications require that this result be above 97.5%; the average result is about 98%. Occasionally the laboratory runs a check for phosphorus on the limestone. In general, phosphorus content is held to less than 0.02 phosphorus pentoxide equivalent; this figure is not significant for calcium cyanamide production since phosphorus contamination interferes only with acetylene generation. Magnesium and sulfur content, however, must be held to low limits to maintain optimum production efficiency (10). The total of magnesium and aluminum compounds present must be less than 2% to produce carbide suitable for calcium cyanamide production (11).

Fluorspar samples from each shipment (1500 tons) are analyzed and usually run between 92 and 94%. Ninety per cent calcium fluoride is considered the minimum permissible assay.

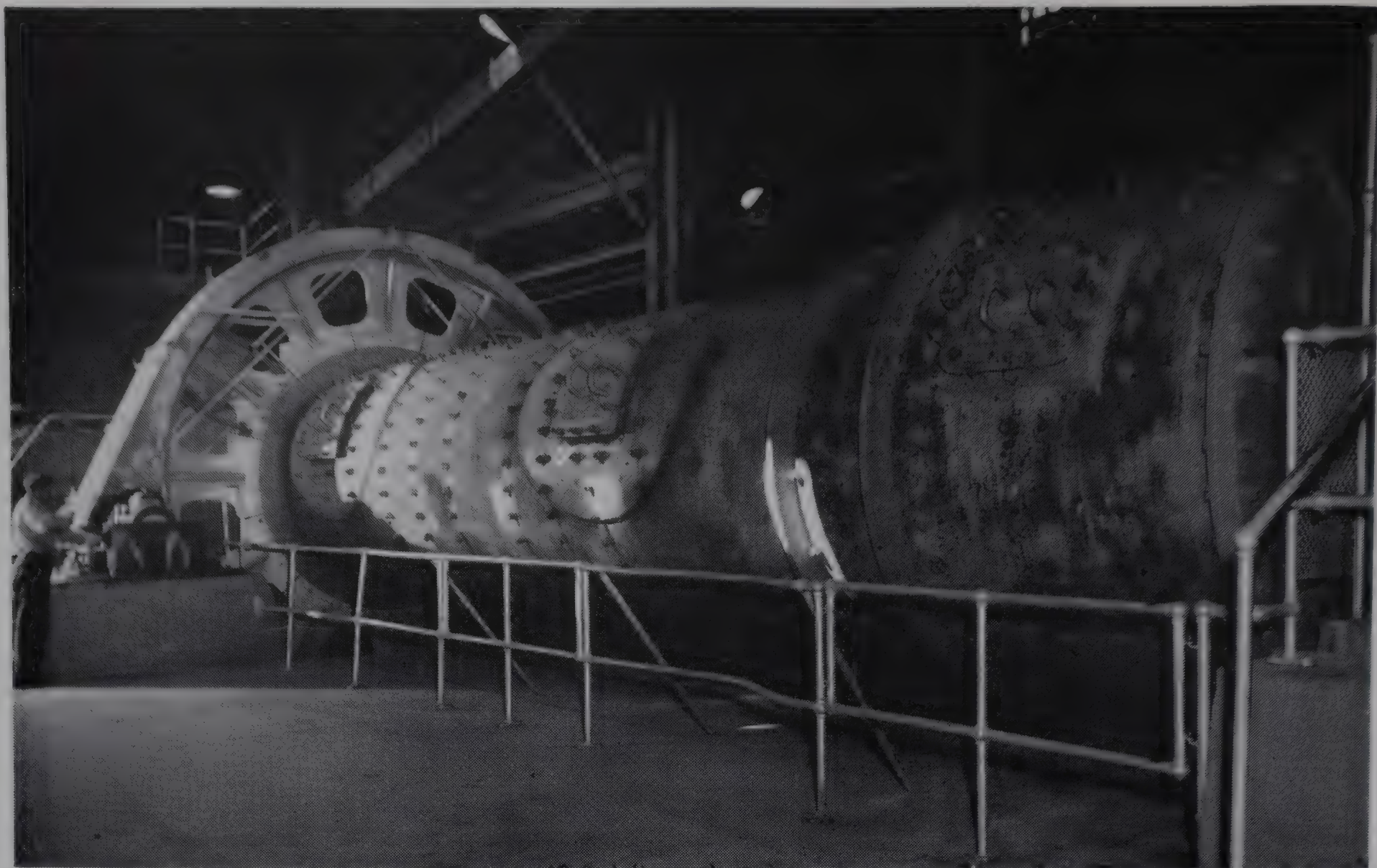
Nitrogen is analyzed three times a shift in the liquid air plant. Minimum specifications call for 99.85% nitrogen. However, these units reliably produce 99.90 to 99.95% nitrogen. A moisture analysis on the nitrogen stream is also run once a day at the oven room, primarily to detect leaks in the lines.

TABLE II. SPECIFICATIONS FOR ROTARY EQUIPMENT

	Residence Time, Min.	Length, Feet	External Diameter, Feet	R.P.M.	Temperature	
					Inlet	Outlet
Coke dryers (2)	35	65	8	3.5	660° C.	110° F.
Lime kilns (7)	60	128	8	1.5	1250° F.	225° F.
Lime cooler	...	40	8	...	2300° F.	1100° F.
Fluorspar dryer	20	25	4	6	1000° F.	300° F.
Oven charge mills (3)	...	36	8	20
Hydrated cyanamide cooler	...	100	6	1.8	120° C.	40-45° C.

The product of the calcium carbide furnaces is sampled every 20 minutes and an hourly composite sample is analyzed for carbide content. A composite sample of the charge to each two calcium cyanamide ovens is also analyzed for calcium carbide. Operators normally expect a drop of about 1.5% in carbide content between the furnace and the ovens.

The crude cyanamide product is analyzed for total nitrogen and residual carbide after the product of each carbide milling (equal to 5 to 30 ovens) has been completed. From these determinations it is possible to determine the efficiency of nitrification. Total nitrogen usually runs 24 to 25%.



Three-Stage Ball Mills Mix Components of Calcium Cyanamide Oven Charge and Reduce It to -100 Mesh

Nitrogen and ash concentrations are determined before and after hydration on each hydration run. The change in the ratio of these two figures will give an indication of nitrogen loss in the operation. Minimum hydrate material is controlled to a minimum of 21% nitrogen; pulverized calcium cyanamide must have not less than 25% ammonia equivalent, not more than 0.1% calcium carbide, and between 3 and 5% oil.

The granular product is analyzed for size on a composite sample each shift. Operating standards require that the material pass 99% through an 8-mesh screen, no more than 2% through a 48-mesh screen, and less than 0.25% through 100-mesh screen. The moisture content of the granular product, after drying, is checked every hour against the standard of less than $1\frac{1}{2}\%$. The mechanical properties of the granules are also determined by testing their resistance to abrasion and to cracking in a moisture-saturated atmosphere at 85°C . Nitrogen analyses are made to ensure that the product contains at least 20% nitrogen.

Safety Precautions

The presence of a very explosive gas, high temperature, and high voltages have exposed the Niagara Falls plant to serious hazards. However, constant safety consciousness in design and redesign has helped to maintain a good record of safety. Much of this record can be credited to a good safety organization and common sense studiously applied.

Epigrammatically the principle behind the handling of acetylene seems to be, "Don't try to control it too much." The instructions to the plant men have been "If at all possible allow an acetylene fire to continue burning. While it is burning it can't build up an explosive concentration." Equipment where acetylene might be expected to form or gather has been equipped with cloth or paper "blowout" sections. Some sections have been blown out in the course of 40 years, and although the noise has

been disconcerting the damage has been slight. Sand is available throughout the plant and carbon dioxide extinguishers are also in use.

As mentioned previously nitrogen blankets are utilized in equipment where carbide is likely to come in contact with water. These spaces are checked for acetylene once a week and before any mechanical work is done on the equipment. If the concentration is found to be greater than 0.5% the entire system is flushed out with nitrogen. The explosive range for acetylene is above 2.5%.

To minimize the fire hazard in the furnace building the electrical transformers are separated from the furnaces by a fire wall through which the bus bars pass by means of fireproof stuffing boxes. Since most of the fires in the plant have been in the transformers this would seem to be a wise precaution.

Personal protection for workers is provided by a rigidly enforced ruling that every person entering the plant area must wear both safety glasses and a head covering. These regulations have reduced eye injuries and skin irritations caused by lime dust and crude calcium cyanamide almost to the vanishing point.

Maximum utilization of the combined common sense of the plant personnel is ensured by a formal committee organization. Each department in the plant holds a monthly safety meeting at which specific safety hazards and safety measures are dealt with. A departmental safety inspector implements such measures as can be accomplished on a departmental level. These inspectors assume their safety responsibilities in addition to their other duties. If the problem transcends the departmental level it is brought to the attention of the Divisional Safety Committee, or working committee, composed of all departmental superintendents. Most remedial measures can be accomplished by this group but problems requiring major operational revisions may be referred to the General Safety Committee composed of the top plant executives and headed by the plant manager.

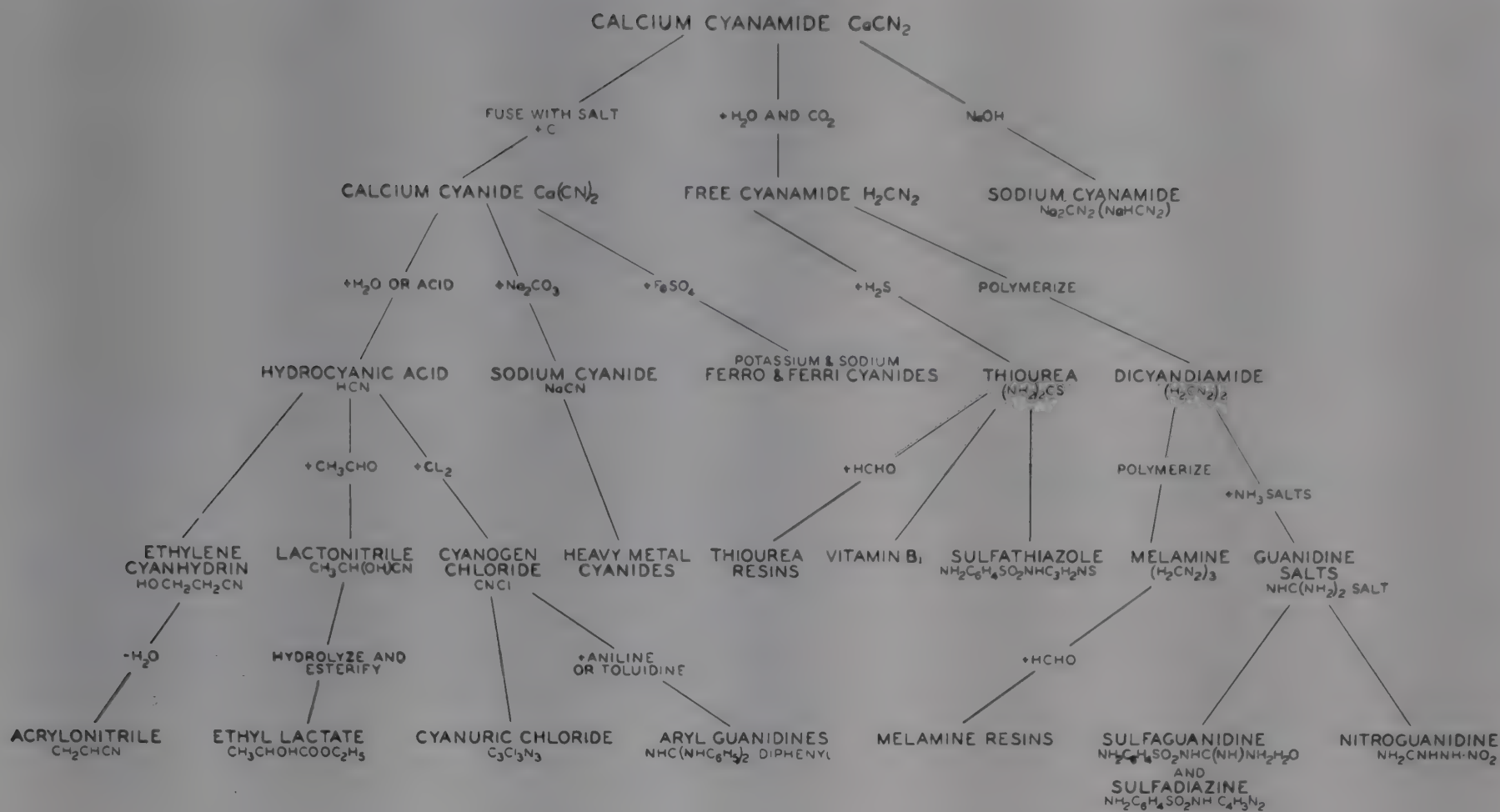


Figure 7. Use of Calcium Cyanamide in Chemical Production

PRESENT MARKETS

The major market for calcium cyanamide is still agricultural, and in this market the largest use is still in fertilizers. Although its cost per unit of fixed nitrogen is higher than that of other common fertilizers it has maintained its sales strength because of certain peculiar properties. One of these properties is its high alkalinity (pH about 12) which makes it especially suitable for use on highly acid soils or as a neutralizer with acidic fertilizers. Another unique advantage of calcium cyanamide is its ability to speed equilibration in mixed fertilizers. Normally such products must be stored for as much as a year to allow all of the components to interreact to equilibrium conditions. The addition of calcium cyanamide to the mix can shorten this aging period to a few days.

Calcium cyanamide itself is actually a herbicide and if applied directly in excessive, strong concentrations to seeds or foliage will have a damaging effect. However, when applied to the soil it hydrolyzes to form lime and urea, and the latter undergoes further hydrolysis to ammonia. Consequently when used as a fertilizer calcium cyanamide must be applied either before planting or well away from plant seeds or roots.

This herbicidal action, however, accounts for the second major agricultural use of calcium cyanamide. It has found wide application for the defoliation of cotton plants to permit machine picking, and it has an increasing use in partial defoliation of other plants to ensure complete sun-ripening just before harvest time.

It is also used in seedbed preparation to sterilize the ground before planting and to hasten the decomposition of crop wastes. Although calcium cyanamide is generally used for these applications the hygroscopic sodium salt is sometimes used in arid climates for defoliation.

The largest chemical use of calcium cyanamide is in the preparation of the dimer, dicyandiamide, called "dicy." The dimer is produced by acidifying the calcium salt to liberate pure hydrogen cyanamide and then dimerizing under mildly alkaline conditions.

Most of the dicy produced by American Cyanamid is further polymerized at high temperature and moderate pressure to produce the trimer, melamine. Melamine goes into plastic resins

which are notable for their superior strength, hardness, and moisture and temperature stability. Most of these resins are used in molding compounds, but substantial quantities are also used to impart high wet strength and other special properties to paper, to provide shrinkage control and crease resistance to wool and rayon, and in the tanning of white leather. Melamine has also found use in wear-resistant laminates and in the formulation of baked finishes for metals in conjunction with other resins.

Another group of derivatives made from dicy are the guanidine salts usually made by fusing dicy with an ammonium salt. Guanidine nitrate made in this way is used in the manufacture of Picrite, a high explosive propellant used in large caliber guns. Guanidine carbonate is used in soaps and synthetic detergents to reduce hygroscopicity and to increase detergency.

Most of the other commercial derivatives of calcium cyanamide are produced by way of calcium cyanide. If a high temperature melt of the cyanamide is quenched, a crude product is produced containing about 50% calcium cyanide. This "black" cyanide is used directly for the cyanidation of ores, especially of precious metals. It is also acidified to yield hydrogen cyanide gas or purified to give high purity calcium or sodium cyanide.

A small quantity of hydrocyanic acid is sold as such, but its major value is also for the production of an abundant family of derivatives. The most important of these is acrylonitrile, which is made by condensation with ethylene oxide to produce ethylene cyanohydrin which can be catalytically dehydrated to acrylonitrile. Acrylonitrile is used principally today for the manufacture of synthetic rubber by copolymerization with butadiene. However many other uses are developing rapidly, the most promising of which is the production of wool-like synthetic fibers from acrylonitrile polymers and copolymers. The widespread interest in these fibers and the number of production plants being built or recently completed indicate that these fibers will soon be commercially important. If the fibers live up to their early promise acrylonitrile could become a major outlet for calcium cyanamide if it can retain its competitive position as a source of cyanide. Acrylonitrile is a chemical intermediate undergoing a wide variety of reactions. One of its derivatives now under development is β, β' -oxydipropionitrile.

Crude calcium cyanide from the cyanamide is also used for the manufacture of sodium and potassium prussiate, used in the manufacture of yellow pigments. Hydrogen cyanide can be chlorinated to produce cyanogen chloride. Although this process accounts for only a small percentage of the total calcium cyanamide production the product is an intermediate for an important group of compounds. Diphenylguanidine and di-*o*-tolylguanidine made from cyanogen chloride are used as rubber accelerators. Cyanuric chloride is a dyestuff intermediate used in the synthesis of yellow dyes and of the so-called "white" dyes or optical bleaching agents.

Hydrogen cyanide is also used to produce small quantities of the solvent ethyl lactate, ethylene cyanohydrin, and acetone cyanohydrin.

FUTURE

Since diversity of application is said to be the key to vitality in a chemical product, calcium cyanamide may be said to be getting healthier all the time. Since most of its present agricultural use is dependent on its own unique properties it can expect continued acceptance in that field, somewhat independent of price relationship. Melamine resins are well established and growing, almost without competition in certain fields. The other chemical uses of the compound and its polymers seem to be expanding and their importance will depend on the applications that can be found for them and the economic balance they can maintain with competing compounds. Much will depend on the ultimate economics of the production of hydrogen cyanide from calcium cyanamide. If this process can maintain its economic position calcium cyanamide will feel the surge in acrylonitrile consumption now beginning. In order to maintain that position it may be necessary to make basic modifications in the 45-year-old process used at Niagara Falls. However, at this writing none of the suggested alternatives seems to offer any advantages to the American producer. Whether the carrot of a large new market will be sufficient incentive to change this situation remains to be seen.

ACKNOWLEDGMENT

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Portable Electrode Used to "Needle" Carbide Furnace When Flow Becomes Sluggish

Man in foreground holds steel reamer which sometimes serves same purpose

- (19) Takeo, Aono, *Bull. Chem. Soc. Japan*, **16**, 92-8 (1941).
- (20) *Ibid.*, pp. 106-14.

Processing Equipment

- (1E) American Blower Corp., 6001 Russell Ave., Detroit, Mich., Sirocco dust collectors.
- (2E) Beaumont Birch Co., 1501 Race St., Philadelphia 2, Pa., Beaumont, Jeffery, and Vulcan crushers, 36 × 48 inches.
- (3E) Birdsboro Steel Foundry & Mach. Co., 1941 Furnace St., Birdsboro, Pa., Buchanan, Type C, carbide jaw crusher.
- (4E) Buffalo Forge Co., 465 Broadway, Buffalo 4, N. Y., 2000 cu. ft./min., 4-stage scrubber.
- (5E) Consolidated Packaging and Mach. Corp., 1900 West St., Buffalo 13, N. Y., Bagpak automatic bagger, Type A (40 tons/hour).
- (6E) *Ibid.*, Type 0-2 scales.
- (7E) Dracco Corp., 4069 East 116th St., Cleveland 5, Ohio, filters.
- (8E) English Electric Co., Catherine, Ont., transformers 1 and 2, 4000 kv.-amp.; 3 and 4, 7250 kv.-amp.
- (9E) Foster Wheeler, 6 Church St., New York, N. Y., Aero coal pulverizers, Sizes F and G (5 and 4 stages).
- (10E) Gurney, Erie Ave. & D St., Philadelphia, Pa., coke and lime weigh scales.
- (11E) Jeffery Mfg. Co., 956 North 4th St., Columbus 16, Ohio, Type B5 hammer mill (8 inch × 15 feet).
- (12E) L'Aire Liquide Soc., Montreal, Can., liquid air machines, 1600 cu. m./hour.
- (13E) Link-Belt Co., 307 North Michigan Ave., Chicago, Ill., 24 × 24 inch Peck-Carrier.
- (14E) Nordberg Standard Mfg. Co., Chase & Oklahoma Aves., Milwaukee 7, Wis., Symons cone crushers (48-inch diameter).
- (15E) Richardson Scale Co., Clifton, N. J., Type GGG-38 weigh hoppers.
- (16E) *Ibid.*, Model HHH, Class 38, 600-pound scales.
- (17E) St. Regis Paper Co., 230 Park Ave., New York, N. Y., weigh hoppers, 1,2-tube horizontal impeller, universal vertical impeller.
- (18E) Tyler, W. S., Co., 3618 Superior Ave., N.E., Cleveland 15, Ohio, Model 39 screens.
- (19E) *Ibid.*, Type 400 screens with two Jeffery vibrating feeders, Types 4 and 5.
- (20E) *Ibid.*, Model 38, hammer screen (4 × 7 feet).
- (21E) *Ibid.*, Model 39, feed screen (4 × 8 feet).
- (22E) *Ibid.*, Tyroc mechanically vibrated Tyler wet screen (4 × 8 feet) No. F-300.
- (23E) *Ibid.*, Model 39, screen (4 × 5 feet).
- (24E) Williams Patent Crusher & Pulverizer Co., 807 Montgomery St., St. Louis 6, Mo., Williams mammoth Jr. No. 8 bar mill.
- (25E) *Ibid.*, Williams universal No. 8 Bar mill.

Cyanides from the Coke Oven

MERRITT L. KASTENS

Associate Editor

in collaboration with

RONALD BARRACLOUGH

Koppers Co., Inc., Kearny, N. J.

Samples of Liquid Hydrogen Cyanide for Analysis Are Taken from Receiving Tanks at Koppers Plant, Kearny, N. J.

THE sulfur shortage is upon us and promises to be around for some time. While the brimstone producers slog through Louisiana swamps seeking new sulfur domes, petroleum refiners are looking at their acid sludges as a possible source of more sulfuric acid; ore refiners are viewing sulfurous stack gases with new interest, and coke oven operators are recalculating the economics of sulfur recovery from their off-gases by long established methods. Surface sulfur deposits, pyrites, and even anhydrite, neglected as long as the easily mined domes held out, are now the focus of intense interest. In other words, sulfur, like gold, is where you find it, and sulfuric acid consumers are missing no bets.

At the same time, hydrogen cyanide, long a slow-moving product commercially, has suddenly acquired new interest with the advent of the acrylonitrile fibers and the discovery of a new nylon process, both of which require the deadly gas as a fundamental raw material. It too has been the subject of intense technical and economic research. In 1948 two primary producers, Du Pont and American Cyanamid, made less than 40,000,000 pounds. Pittsburgh Coke and Chemical recovered less than 1,000,000 pounds from coke gases. The 1948 processes were based on sodamide, formamide, and cyanamide. By the end of this year three new primary producers, Rohm & Haas, Carbide and Carbon, and Koppers, will be in the picture and with expansion by the original

two producers will boost total production to close to 95,000,000 pounds. Next year Monsanto will get into the act and Du Pont's mammoth 60,000,000-pound plant at Memphis, Tenn., will come on stream; Rohm & Haas and American Cyanamid will expand again to bring the total output to at least 200,000,000 pounds. All this new capacity, with the exception of the American Cyanamid expansion, which will use the cyanamide process, will utilize a reaction between methane and ammonia. All but one of the other new installations will introduce natural gas and ammonia into a reactor and apply high temperatures to make the reaction go to completion. The one exception is the Koppers plant. The Koppers people, like all coke makers, know that this reaction occurs spontaneously in a coke oven. High temperature coke oven gases contain about 60 grains of hydrogen cyanide per 100 cubic feet or about 0.7 pound per ton of coal coked. Disposal of this hydrogen cyanide has actually been a problem for almost as long as coke has been made. Usually the hydrogen cyanide has been decomposed, reacted to produce another product, or simply discharged to the atmosphere or to the sewers. A few producers in Europe and Pittsburgh Coke and Chemical in this country have recovered it as the pure gas, but the processes were not attractive economically, particularly when the market for the material was none too enthusiastic.

Now obviously that situation has changed. The market is strong and appears to be in for a long period of expansion. Furthermore the market for sulfuric acid, which can be produced from another coke gas contaminant, hydrogen sulfide, can only be described as desperate. At this fortuitous point Koppers is developing a process for recovering both hydrogen cyanide and hydrogen sulfide from coke oven gases and has a full scale plant in operation. Such a recovery technique could potentially add 60,000,000 pounds to the annual supply of hydrogen cyanide if it were adopted by all coke oven operators (14).

The potential sulfuric acid production that could be effected by this means is more difficult to estimate since it will depend on the sulfur content of the coal processed into coke, but at least it may be said that full hydrogen sulfide recovery should make the coke operators independent of outside sulfuric for their ammonia sulfate operations. Average coal should produce 8 to 10 tons of 100% sulfuric acid per 1000 tons of coal carbonized. Assuming a conservative 100,000,000 tons of coal coked in by-product ovens in the United States each year this would yield an impressive 1,000,000 tons of acid. Some of this is of course already being recovered by older methods.

Removal of hydrogen sulfide from off-gases is actually an old story to coke oven operators. The gas is apparently formed quite easily by the reduction of the sulfur-containing constituents in the coal and is produced in a greater or lesser extent in all carbonizing operations.

Many effective processes, from the old boxes of wood chips mixed with iron oxide to the current thioarsenate or alkali absorbers, have been used for its removal (9).

HYDROGEN CYANIDE RECOVERY PROCESSES

The special value of the Koppers process lies in its recovery of hydrogen cyanide. Cyanides as such are not present in coal. They are never formed in low temperature carbonization processes. The process by which cyanide is formed from hydrocarbons and ammonia has not been fully determined; it obviously requires high temperatures and probably involves one or more of the following reactions (12, 13).

	K cal.
$C_2H_2 + 2NH_3 = 2HCN + 3H_2$	-28.0
$C + NH_3 = HCN + H_2$	-39.5
$CH_4 + NH_3 = HCN + 3H_2$	-60.0
$C_2H_4 + 2NH_3 = 2HCN + 4H_2$	-63.0
$CO + NH_3 = HCN + H_2O$	-10.0

No effective catalysts have been discovered for these reactions.

Regardless of the source of the hydrogen cyanide it is desirable to remove it from some gas streams even if it is not recovered, as cyanide forms complexes with iron and consequently is mildly corrosive to steel equipment. In installation where iron oxide is used to remove hydrogen sulfide the elimination of hydrogen cyanide is especially important because it reacts with the iron oxide to produce a solid deposit of iron complexes which soon clogs the boxes.

Many processes have been devised and are used to eliminate cyanide. However, few of those that have found commercial application have recovered the gas in an unreacted form, primarily because there has been only a limited market for pure hydrogen cyanide in the past. Before World War I British, German, and American coke makers were scrubbing their off-gases with alkali solutions and recovering various iron-cyanide complexes from the solution (2, 3, 6, 10, 11, 18, 23). Some of these processes give excellent recoveries and are still in use. Cyanide has also been recovered in nickel and copper complexes and in ammonia-iron compounds (4, 5, 8). In recent years in the United States, it has been recovered as a thiocyanate, usually by reaction

with an ammonium sulfide complex to produce ammonium thiocyanate.

Shortly before World War II a process was introduced in the United States in which the cyanide is reacted with iron sulfate and lime to precipitate calcium ferrocyanide (19). This process found large scale application at the Pittsburgh Coke and Chemical plant at Neville Island, Pa. It has now been superseded by a plant built in 1942 which uses a process very similar to the Koppers installation to be described here. In fact it employs identical equipment for the initial removal of cyanide and sulfide from the coke gas stream. The major deviation is in the final separation of hydrogen sulfide from the hydrogen cyanide solution. The Neville Island plant requires several steps for this operation whereas Koppers accomplishes it in a single stripper-rectifier column.

The hydrogen cyanide removed from coke oven gases has in some cases been destroyed by reaction with permanganate. In other instances the thiocyanates produced by the recovery system have been intentionally decomposed by bacterial cultures. Many processes have been suggested and several employed in the past for the conversion of cyanide into more readily marketed ammonia (1, 15). However, none of these processes offered any appreciable economic advantages. Their major function was the control of pollution and reduction of corrosion.

Polymerization

Lack of enthusiastic markets has not been the only deterrent to the recovery of hydrogen cyanide. Pure hydrogen cyanide, particularly when in the liquid state, has a disconcerting tendency to polymerize explosively, unless properly stabilized. If the polymerization proceeds slowly as it does in dilute aqueous solutions of hydrogen cyanide, there is little decomposition into the constituent elements. The polymer has a smaller percentage of nitrogen and hydrogen than hydrogen cyanide; a typical analysis is 3.4% hydrogen, 46.15% carbon, and 50.45% nitrogen (22) as compared with 3.7% hydrogen, 44.5% carbon, and 51.85% nitrogen in hydrogen cyanide. The excess nitrogen and hydrogen are liberated as ammonia.

The reaction is strongly exothermic and is catalyzed by alkaline environments. Consequently the liberation of ammonia makes the reaction autocatalytic if it is not immediately neutralized. The autocatalytic action makes the reaction tend to "run away" and under such a situation the heat liberated partially decomposes the polymer into elemental gases which are expanded with explosive violence.

The structure of the polymer—a black, semicrystalline material—is complex and apparently varies somewhat with the conditions under which it is formed. The linkage probably involves an opening of the carbon-nitrogen triple bond, although it has been suggested that only the isocyanide form, $H-N\equiv C$, is subject to polymerization. Under some circumstances the polymer exhibits a deficiency rather than an excess of carbon. This latter behavior has been attributed to the incorporation of hydrocarbon molecules. When the polymer is formed in the presence of sulfides it usually will include substantial quantities of sulfur which suggests the possibility that a copolymer of sulfide and cyanide has been created. The poisonous nature of hydrogen cyanide gas has apparently discouraged intensive studies of the polymer-forming reaction.

It is believed that pure hydrogen cyanide will not polymerize in this fashion but will form a trimer of fixed composition. However, such a possibility is not of commercial importance. The commercial material will polymerize spontaneously even in acidic environments, but the rate of the reaction under such conditions is negligible. Consequently the established practice has been to stabilize hydrogen cyanide by the addition of inorganic acids. Phosphoric acid, 0.2% by weight, has been the most common additive, although sulfuric and other acids have been used. The added acid merely reacts with the ammonia evolved

by the polymerization reaction and holds the rate of the reaction at its nominal minimum.

Maintaining stable conditions throughout the steps of any reasonably complex process has been a difficult problem, and earlier coke makers uniformly solved it by converting the poisonous and potentially explosive gas into some more innocuous compound as soon as possible. The forerunner of the Koppers plant, described in this article, experienced an explosion caused by a run-away polymerization in 1949. However, in building the present plant engineering improvements have been incorporated

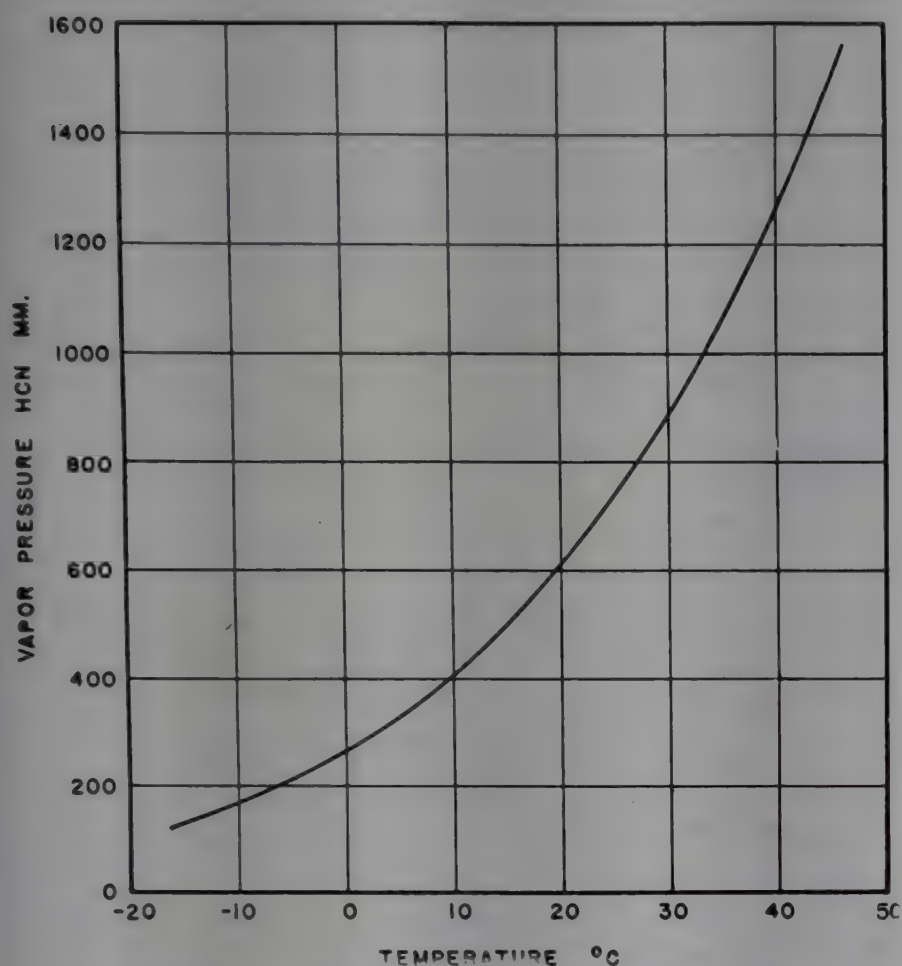


Figure 1. Vapor Pressure of Hydrogen Cyanide

that ensure continuous inhibition in both liquid and vapor phases at all points in the process stream. The acid inhibition of the cyanide polymerization has been known for some time. It is primarily engineering development that has made the Koppers process practical at a time when new market activity is economically attractive.

KEARNY, N. J., PLANT OF KOPPERS CO., INC.

The 220 coke ovens at Kearny produce about 48,000,000 standard cubic feet of gas a day. As this gas comes from the ovens it passes immediately through water sprays which condense the tars and dissolve about 10% of the ammonia present. Essentially no hydrogen cyanide is lost in this water scrubbing because at the temperature of the "flushing liquor" (75° C.), the vapor pressure of hydrogen cyanide is so high that solution in the water is negligible (Figure 1). About 300,000 gallons of this flushing liquor pass through the sprays every hour. It is collected from the gas mains and held in settling tanks to separate the tar and aqueous layers. The tars are decanted off and refined in another section of the Kearny plant. Most of the aqueous liquor from the settling tanks (280,000 gallons per hour) passes through heat exchangers which supply the heat required to desorb the gases in the gas "purification" unit. From the heat exchangers the water is recycled to the sprays in the coke oven gas outlets. The flushing liquor picks up some extra water from the coke oven gases. This excess is drawn off the recycling system and fed to a stripping still which removes the dissolved ammonia. The ammonia recovered is returned to the gas stream. The water is discarded.

The coke oven gas stream is cooled to 80° C. and saturated with

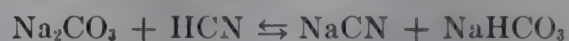
water vapor by the water sprays. It passes through a cooler which precipitates out the residual tars and is then bubbled through a tower containing dilute sulfuric acid; the acid reacts with the ammonia present to form ammonium sulfate which is subsequently precipitated and recovered. Movement of the gases from the coke ovens through the cooler and ammonia scrubber and into the purifying units is accomplished by centrifugal gas pumps located between the cooler and the acid tower.

Absorption of Hydrogen Cyanide, Hydrogen Sulfide, and Carbon Monoxide

The tar- and ammonia-free coke oven gas contains about 0.48 volume % of hydrogen sulfide and 0.13 volume % of hydrogen cyanide. These gases along with carbon dioxide (Figure 2) are scrubbed out by a dilute solution of sodium carbonate in the Koppers unit. Organic absorbents, notably sodium phenolate (20) and the alkynolamines (14), are used to absorb hydrogen sulfide from natural gas, refinery gas, and producer gas. However, these are not adaptable to coke oven gases because they will react with the hydrogen cyanide present and lose their absorbing efficiency. Other hydrogen sulfide removal systems used in the coke industry involve reactions between the sulfide and the absorbent so that the hydrogen sulfide cannot be recovered unchanged. Some of these systems recover finely divided molecular sulfur, but this product is usually sold as an agricultural chemical rather than used for sulfuric acid production.

When these other purification systems are used the hydrogen cyanide either remains in the fuel gas, or it is recovered and returned to a fuel gas line. In a few instances where pollution problems are not acute it may be discharged to the air or to the sewer as an aqueous solution.

In the vacuum carbonate process the coke oven gas passes countercurrent to a stream of 6 to 7% aqueous sodium carbonate in an absorber tower packed with West Virginia spruce hurdles (Figure 3). Gas feed is at a rate of 2,300,000 cubic feet per hour. The alkaline absorbent is fed at 32,000 gallons per hour and leaves the tower at 53° C. The pressure in the absorber is about 50 inches of water gage maintained by gas transfer pumps. The absorption involves the reactions



The overhead from the absorber contains the light oil and naphthalene fractions as well as the gaseous hydrocarbons of the

TABLE I. CHEMICAL AND UTILITY REQUIREMENTS PER DAY

Coke oven gas feed, stand. cu. ft./day	50,000,000
Vacuum purification (Na_2CO_3), lb.	400
HCN recovery, gal.	
H_2SO_4 (93%)	2.52-2.7
H_3PO_4 (85%)	0.25-1.0
Sulfur recovery, tons	20
165-lb. steam, lb.	
Vacuum purification	
HCN recovery	40.0
Sulfur recovery (heat recovery gives net gain)	(+150,000)
15-lb. steam, lb.	
Vacuum purification	9,600
HCN recovery	2
Sulfur recovery	...
Brackish water, gal.	
Vacuum purification	1,844,000
HCN recovery	65.5
Sulfur recovery	50,000
City water, gal.	
Vacuum purification	187,000
HCN recovery	45.5
Sulfur recovery	22,000
Electrical power, kw.-hr.	
Vacuum purification	7,880
HCN recovery	.45
Sulfur recovery	4,000
H_2SO_4 (100%), tons	86
HCN (98.5%), lb.	2,940

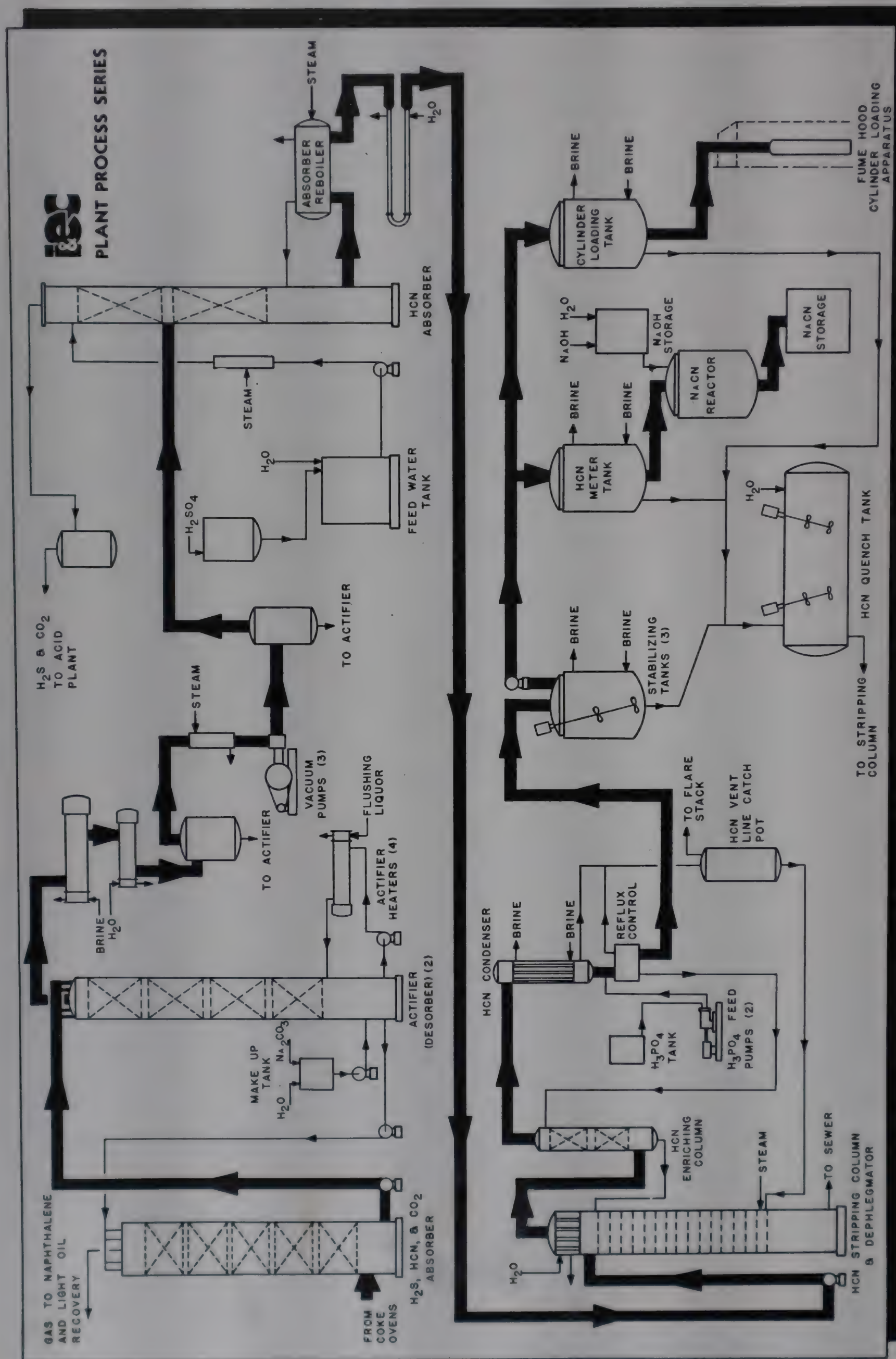


Figure 2. Flow Sheet for the Production of Hydrogen Cyanide at the Kearny, N. J., Plant of Koppers Co., Inc.

original gas; 93% of the hydrogen sulfide, 85 to 90% of the hydrogen cyanide, and virtually all the carbon dioxide have been removed. The residual hydrogen sulfide is removed by passing it through boxes of wood chips impregnated with iron oxide.

Desorption

The alkaline solution from the bottom of the absorber is sprayed into the tops of two parallel desorption columns or "actifiers." The absorption reactions in the liquid purifier system are all reversible, and equilibrium is influenced by pressure and temperature. In the Seaboard process, which was the predecessor of the present operation, desorption was accomplished by

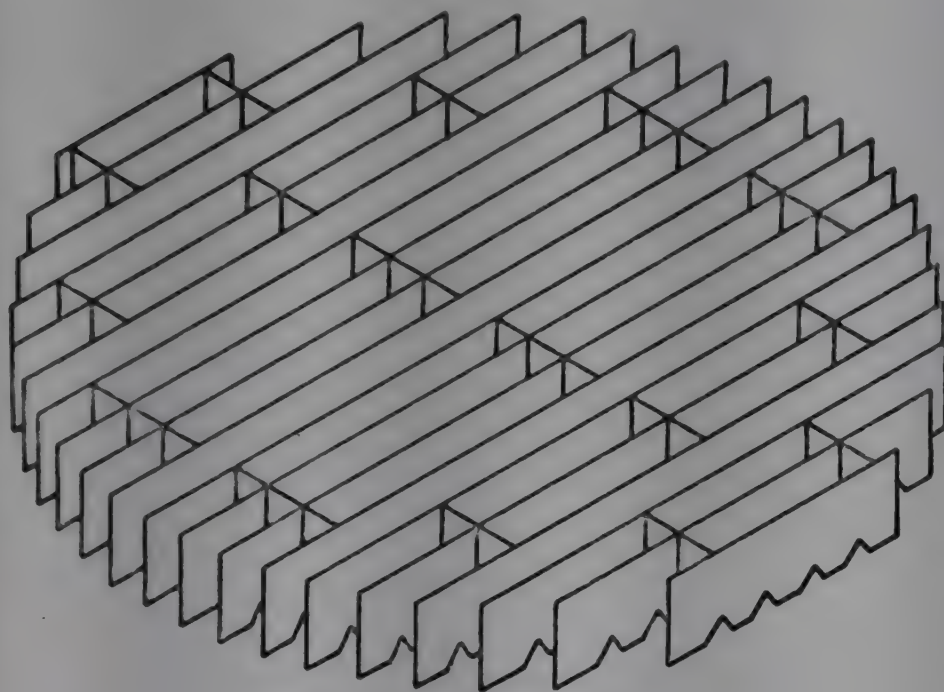


Figure 3. Hurdle Packing

heat and aeration of the solution with air or clean fuel gas (17). However, such aeration converted some of the sulfide to thio-sulfate and most of the cyanide to thiocyanate, thus preventing their recovery as gases. The technique now used at Kearny employs water vapor to strip the gas from the absorbent and maintains a vacuum on the system to reduce the heat required to produce the water vapor (21). At the operating pressure of about 4.2 inches of mercury absolute, the volume of vapor required to strip the solution is about the same as it would be at atmospheric pressure, but the weight of the vapor and hence the heat required to produce it is less than one fifth as great. The bottom sections of the desorption columns act as reservoirs for the absorbent. About 2000 gallons are held in each. The total volume of absorbent in the purification system is about 8000 gallons. The absorbent in the bottoms of the desorbing towers is pumped at about 300,000 gallons per hour through exchangers heated by the flushing liquor from the coke gas mains. These exchangers supply all the heat required by the desorption operation. The actifiers operate at about 53° C. An automatic level control operates the outlet valve of a pump that recycles the stripped carbonate solution from the reservoir to the head of the absorber. Return of sulfide or cyanide to the absorber would reduce the absorbing efficiency of the carbonate solution and result in excessive carry-over of these gases in the fuel gas stream.

Liquid carry-over from the actifier towers is caught in knockout drums (Figure 4) and returned to the actifier bottoms. However, some absorbent is lost from the top of the absorber column. Under normal operating conditions this loss amounts to about 2400 gallons of water and 400 pounds of sodium carbonate a day.

The gas from the actifiers is about 55% hydrogen sulfide, 15% hydrogen cyanide, and 25% carbon dioxide. A small amount of inert gas, primarily nitrogen, from air leaks in the system and some hydrocarbons and hydrogen may bring the total of minor constituents to as much as 5%. The percentage of hydrogen

sulfide in this stream is relatively low since the Kearny plant uses low sulfur (1.0%) West Virginia coals. High sulfur coals contain as much as 5% sulfur, about half of which would be released as hydrogen sulfide to give a mixed gas from the actifiers with as much as 75% hydrogen sulfide. Gas from high-sulfur coals will release more carbon dioxide from the carbonate solution in the actifiers, so that the percentage of hydrogen sulfide in the gas stream does not become as high as might be expected, although the total volume of gas is increased substantially. The percentage of hydrogen cyanide formed is little affected by the composition of the coal being coked.

The desorbed gases pass through a sheet-and-tube condenser cooled with salt water, which reduces the temperature to 38° C., and then through a smaller, fresh water-cooled condenser, which cools it to 21° C. This double condenser system is used because the salt water coolant taken from the brackish inlets adjacent to the plant attains temperatures as high as 31° C. in the summer whereas the temperature of the city-supplied fresh water seldom exceeds 10° C. A knockout drum after the condensers removes entrained water. The condensers and the knockout all drain back to the actifier reservoir. The gas stream containing hydrogen sulfide, hydrogen cyanide, and carbon dioxide passes from the knockout through a short length of steam-jacketed pipe, used as a conditioner in cold weather, and into the reciprocating pumps which maintain the vacuum in the actifier column. There are three of these single-stage, horizontal pumps each with a capacity of 1700 cubic feet per minute, but only two are on the line at any one time.

The vacuum carbonate operations are conducted in the old gas purification area of the plant. They are all relatively standard and may be found in other installations. Lack of space around the existing purification unit necessitated location of the hydrogen cyanide and hydrogen sulfide recovery unit in a new area of the site, about 0.25 mile away. The gas from the carbonate absorption operations is piped to the new area through a 4-inch, carbon steel main by the pressure of the vacuum pumps.

Hydrogen Sulfide and Hydrogen Cyanide Recovery

When the gas stream arrives at the new installations, it is introduced into a knockout drum which removes entrained liquid or condensables from the previous operations. There is actually so little drainage from this drum that only biweekly tapping is required. Steam coils in the bottom prevent freezing in cold weather and drive any dissolved hydrogen cyanide or hydrogen sulfide from the collected water before it is discharged.

From the knockout drum the gas stream goes directly to the center of the hydrogen cyanide absorbing column. Twenty-foot

TABLE II. MATERIALS BALANCE FOR HYDROGEN CYANIDE RECOVERY OPERATION

Feed, lb./hour		
HCN	162	
H ₂ S	605	
CO ₂	277	
Others	56	
City H ₂ O	8350	
		9450
Products, lb./hour		
Overhead from absorbers		
H ₂ S	605	
CO ₂	277	
Others	56	
		938
Overhead from stripping still		
HCN	160.4	
H ₂ O	3.4	
		163.8
Stripping still bottoms		
HCN	1.6	
H ₂ O	8346.6	
		8348.2
		9450

sections above and below the inlet are packed with Berl saddles. Water, acidified with sulfuric acid to pH around 3.0 and heated to 30° C. by direct injection of 165-pound steam is introduced (6E) at the head of the column. Gas flow in the absorber is 12,000 cubic feet per hour. The flow of acid solution between 900 and 1100 gallons per hour keeps the hydrogen cyanide content of the overhead discharge below 10 grams per 100 cubic feet (0.02% by volume). Heating the absorbent prevents naphthalene from precipitating out and reduces the vapor velocity in the column.

The packed section of the absorber column below the inlet acts as a rectifier to remove hydrogen sulfide. The solution going into this rectifier section is essentially saturated with hydrogen sulfide (about 2 grams per liter). The rectifier section operates with a top temperature of 30° C. and a bottom temperature of 95° to 100° C.

Sulfuric Acid Production

Hydrogen sulfide and carbon dioxide pass out the top of the absorber, through a knockout drum to remove entrained water picked up in the absorber, and then are sent to the adjacent contact sulfuric acid plant. This gas stream is fed directly into a jet in the acid plant combustion chamber. It contains about 65% hydrogen sulfide, 30% carbon dioxide, and 5% other gases. The carbon dioxide and other inerts in the stream are carried through and ultimately discharged from the vents of the sulfur trioxide absorbers.

The acid plant used at Kearny is a 10-year-old standard type of contact unit. Most modern contact acid plants use a "dry"

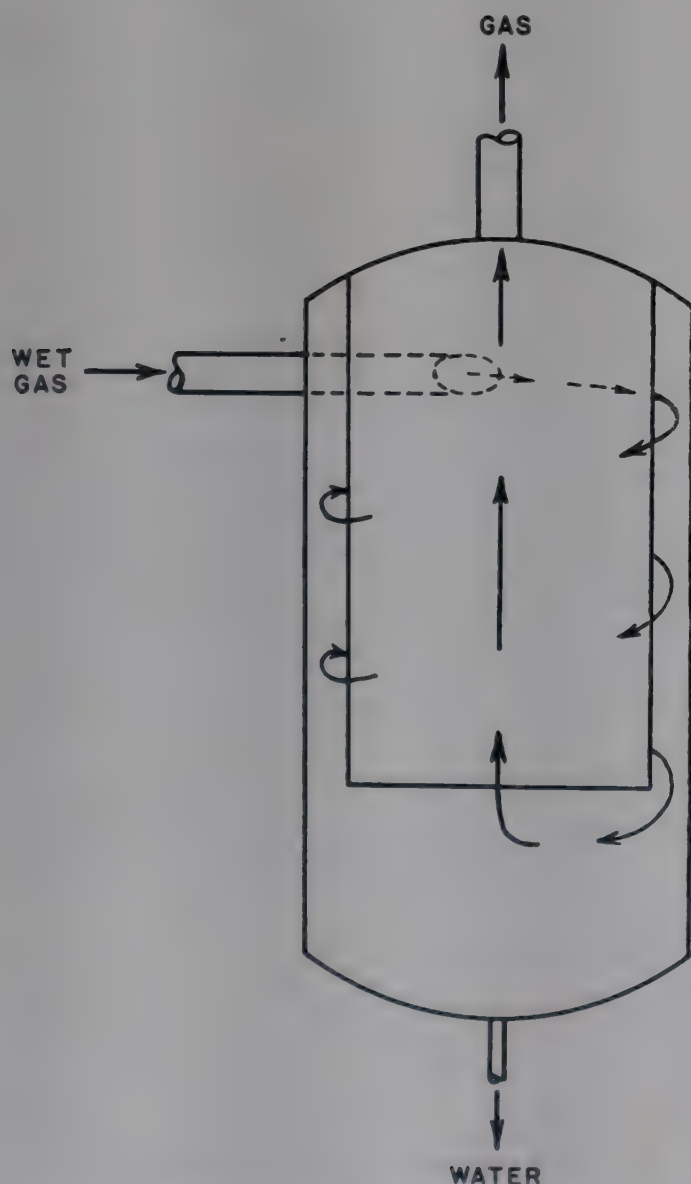


Figure 4. Knockout Tank

process—that is, the combustion air is dried before it is admitted into the burner, and the water content of the gases is kept at a minimum throughout the process. However, since the burning of hydrogen sulfide produces water it is impossible to use this type process with the gas recovery system. Consequently, the Kearny operation uses a "wet" process in which the sulfur dioxide gas is

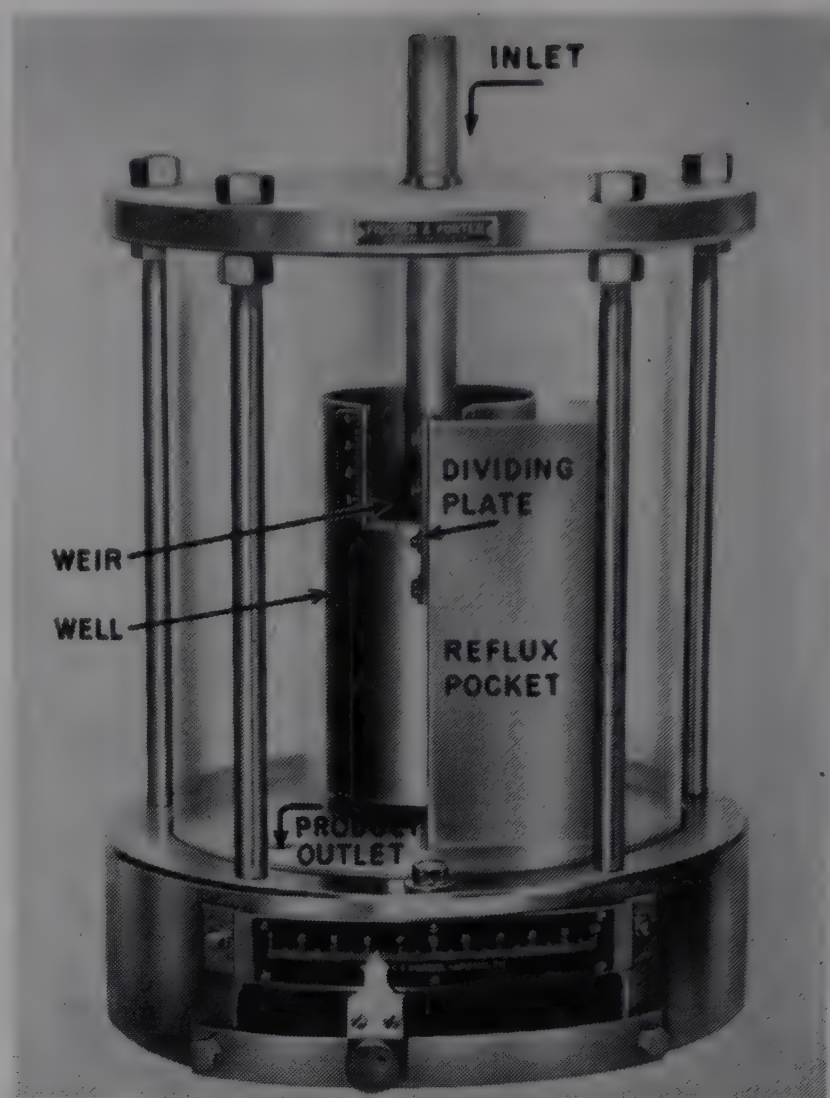


Figure 5. Ratoweir

dried between the burner and the converters. The new "quench converter" type contact plant in which the conversion is done on the wet sulfur dioxide gas would be particularly applicable to the use of hydrogen sulfide in sulfuric acid manufacture (16).

According to experience at the Kearny plant, it would be possible for the recovery operation described here to produce all the sulfuric acid required to convert the ammonia recovered from the coke gas into ammonium sulfate, if a coal of average sulfur content was being coked. However, the generally accepted minimum economic size for a sulfuric acid plant is about 100 tons of acid per day. A plant of that size would require gases from a very large battery of coke oven—much larger than that at Kearny. About 60% of the acid produced at Kearny is shipped outside the plant. Consequently, a separate burner jet in the acid plant combustion chamber burns molten sulfur to supplement the hydrogen sulfide fuel. Hydrogen sulfide burns with a much hotter flame than sulfur, and this higher temperature must be taken into account in designing an acid plant to burn all or part hydrogen sulfide. The Kearny acid plant feeds about twice as much sulfur as hydrogen sulfide. This results in a temperature of about 1150° C. in the burner compared to about 950° C. in a conventional unit burning all sulfur.

Hydrogen Cyanide Separation

The water solution of hydrogen cyanide from the bottom of the hydrogen cyanide absorber-rectifier is drawn into a shell-and-tube reboiler. Steam to the reboiler tubes is automatically controlled and maintains a pressure drop equal to 5 to 8 inches of water through the rectifier section. Steam and the last traces of hydrogen sulfide stripped from the hydrogen cyanide solution return from the reboiler to the absorber-rectifier column. About 1000 pounds of steam per hour are required to obtain optimum performance on the rectifier. An automatic level controller regulates the flow of solution from the reboiler into a water-cooled, double-pipe, hairpin heat exchanger where it is cooled from 90° to 80° C. to prevent vapor binding in the transfer pumps.

The absorber operates at 5 pounds per square inch pressure maintained by a back pressure controller on the overhead while the

Gas Recovery Plant and
Sulfuric Acid Plant

stripper is at atmospheric pressure so that cooling is also necessary to eliminate the possibility of flashing in the stripper.

The cooled stream of what is called "foul solution," containing about 2% hydrogen cyanide, is pumped (6E) to the top of a ten-tray stripping still. About 1100 pounds per hour of 165-pound steam are introduced directly into the bottom of the tower to effect the distillation. Water at 100° C. containing less than 0.02% hydrogen cyanide is discharged from the bottom of this column by an automatic level control and sent to the sewer. The overhead stream at 85° C. passes through a small water-cooled, vertical tube condenser called a dephlegmator. Cooling the vapor stream at this point allows the enriching column to operate at a much lower reflux ratio. The condenser also prevents surges of cyanide from flooding the enriching column and reduces the load on the hydrogen cyanide condenser. The vapors leave the dephlegmator, at 55° C., containing about 50% of water. They pass into an enriching column, packed with 1/2-inch ceramic Berl saddles, which completes the removal of water from the stream. The bottoms from the enriching column are returned to the top of the stripper. The enriched hydrogen cyanide vapor at 26° C., containing about 98.5% hydrogen cyanide, is chilled to 5° C. in a brine-cooled, shell-and-tube condenser to avoid polymerization. This liquid hydrogen cyanide stream then passes into an adjustable refluxing weir (Figure 5) (2E). Under normal conditions about 50% of the liquefied, stabilized hydrogen cyanide is returned to the top of the enriching column as a reflux. A con-

tinuous specific gravity meter on the reflux line provides a constant check on the purity of the product.

About 0.1% of phosphoric acid (0.0235 gallon per hour) is added to the hydrogen cyanide on the refluxing apparatus to inhibit polymerization both in the product and in the stripping still. The phosphoric acid is commercial grade and is pumped from the 50-gallon storage tank by two parallel, positive displacement, pulsating diaphragm type metering pumps (7E).

Stabilizing

The liquid hydrogen cyanide product is piped to one of three brine-jacketed, 250-gallon, receiving tanks. The three tanks are used sequentially and will each hold about 8 hours' production. The tanks are stirred with a double-propeller agitator driven by a 1-hp. motor at 350 r.p.m. As soon as a tank is filled it is analyzed for stabilizer content. If the analysis shows less than 0.2% of phosphoric acid, acid is added to make up the difference. Stabilized hatches are pumped (8E) to a meter tank, brine-cooled to about 2° C. From the meter tank the liquid hydrogen cyanide may be diverted either to the cylinder-filling department or to the reactors in which sodium cyanide is prepared. If it is to be shipped as liquid hydrogen cyanide it is transferred to a brine-cooled (2° C.) loading or surge tank from which it is drawn directly into chilled shipping flasks.

At present Koppers is not shipping any cylindereed hydrogen cyanide from Kearny. The entire output of the plant is sold as 30% aqueous sodium cyanide solution. Processing to this end

product eliminates the fire and explosion hazard of storage and handling of liquid hydrogen cyanide.

Sodium Cyanide Production

To make the sodium cyanide solution about 400 gallons of commercial 50% aqueous caustic solution are introduced into a reactor and diluted with water to 23 to 29% depending on the atmospheric temperature. Hydrogen cyanide is then introduced from the meter tank through a dip pipe at a decreasing rate until almost all the sodium hydroxide has reacted. The rate of addition of the cyanide must be controlled carefully and the reactor charge agitated vigorously to ensure that the hydrogen cyanide introduced reacts immediately with sodium hydroxide. If a local concentration of sodium cyanide should build up around the dip pipe, free hydrogen cyanide would collect momentarily and, in the alkaline solution, would begin to polymerize. Although the polymerization would not progress very far before the hydrogen cyanide would be reacted, enough polymer would form to discolor the sodium cyanide solution.

As the sodium hydroxide is depleted by reaction to sodium cyanide the added hydrogen cyanide does not react as quickly and the rate of addition must be reduced. The progress of the reaction is followed by frequent density determinations until the end point is approached. The final addition is calculated from a titrimetric analysis. The product contains about 2% free sodium hydroxides to ensure that the stoichiometric point is not exceeded.

Measurement of solutions is by visual observation of calibrations on the feed tanks. The standard batch produces 1000 gallons of 28 to 35% sodium cyanide varying with the time of year. In the winter the low concentrations must be used to avoid solidification in transit. In the warmer months the concentration is increased to save on shipping costs. All billing is on a sodium cyanide content basis.

Performance

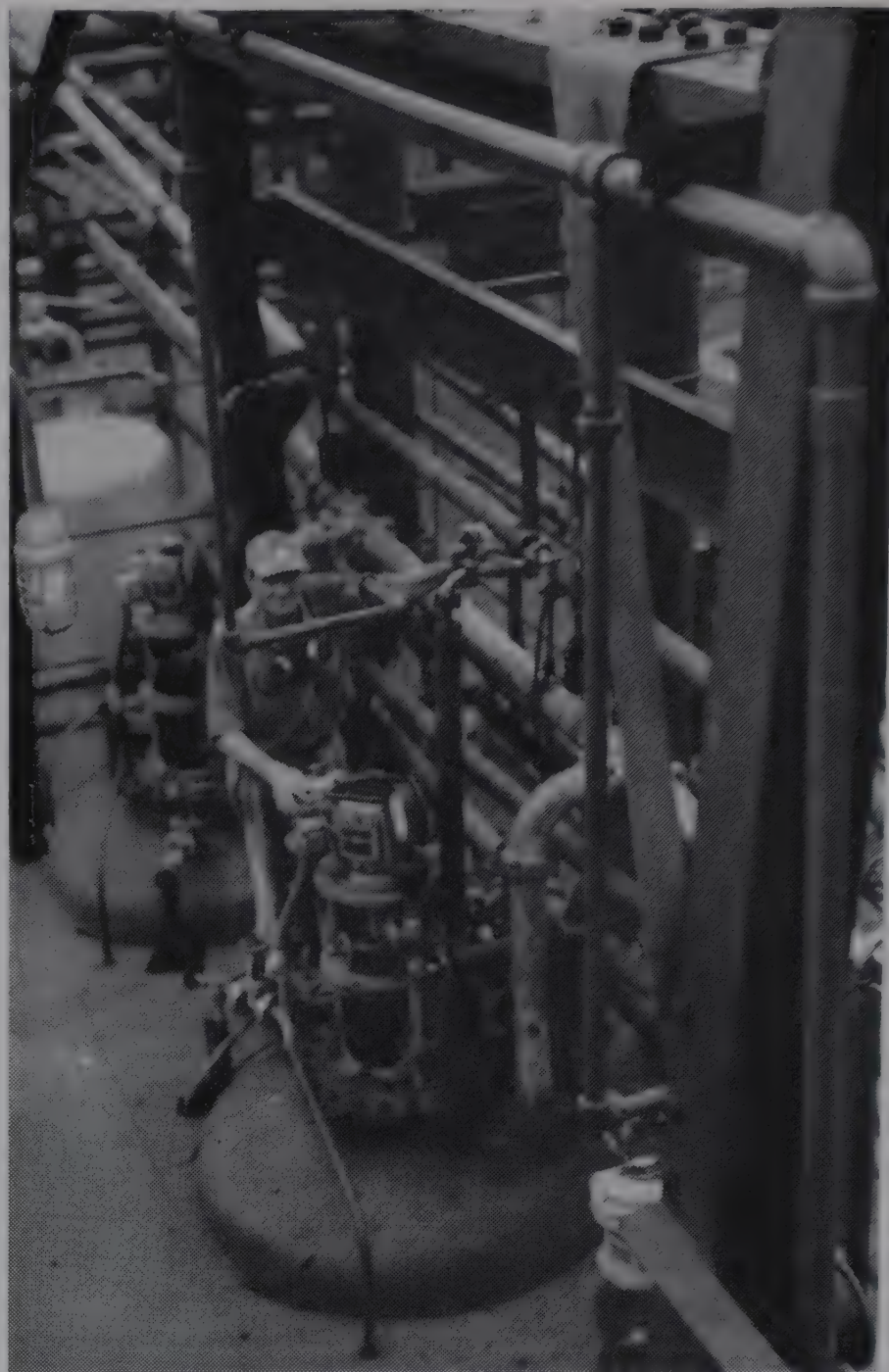
The Kearny plant produces about 172 pounds per hour of 98.5% hydrogen cyanide from a feed rate of mixed gases of about 12,000 standard cubic feet per hour.

Under optimum conditions the yield of hydrogen cyanide calculated on the feed to the hydrogen cyanide absorber is about 99%. The major product loss is incurred in the maximum of 1.6 pounds per hour of hydrogen cyanide that is lost in the bottom discharge of the stripper column.

Recently the operators of the plant discovered a serious corrosion problem in the absorber and the lower sections of the stripping still. Although the Type 304 stainless steel used for this equipment appears to be adequately resistant to the necessary concentrations of sulfuric when tested in the laboratory, rapid corrosion has been experienced in actual use. It is possible that this corrosion was caused by experimental runs in which acetic acid or other supplementary inhibitors were added to the dilute acid absorbent. If acetic acid is used as a vapor phase inhibitor it may be necessary to find some more resistant material for the construction of the process vessels. However, there is some possibility that reducing the acidity of the absorbent will eliminate the corrosion problem without impairing the absorbing efficiency of the column.

Previously the absorbent was held at pH's as low as 2.3. It is hoped that an acid solution with pH as high as 3.5 will give the same absorbing efficiency.

Polymer formation in the equipment containing pure hydrogen cyanide or aqueous solution of hydrogen cyanide in concentrations greater than 50% by weight has apparently been completely eliminated by proper engineering design and the addition of phosphoric acid inhibitor. However, a slow accumulation of polymer has occurred in the absorber section of the recovery plant where dilute solutions of hydrogen cyanide are involved. Although the formation is slow and does not entail any explosive



Transfer Pumps

Submerged mounting of pumps and off-center introduction of agitator as seen from top of receiving tanks

hazard it affects operating conditions and has necessitated several shutdowns. This polymer formation seems to be primarily caused by dead spots in the equipment which are not continually flushed by fresh solution. Under such conditions the acid inhibitor is gradually exhausted by reaction with ammonia released by slow polymerization, and the autocatalytic phase of the polymerization is attained. Vapor phase inhibition of the polymerization by the introduction of sulfur dioxide solutions and sulfur dioxide gas has not been effective in eliminating the polymer formation. Acetic acid added to the sulfuric acid in the absorbent for the same purpose also seemed to have little inhibitory effect on the polymerization and may have increased the corrosion of the absorber. The most promising remedy for this condition seems to be a modification of the internal arrangement of the equipment involved to ensure that fresh solution reaches all surfaces continuously.

Operating experience has shown that the simplest and most straightforward start-up procedure is both the safest and most efficient. In lighting off the plant the absorber is first purged with steam to eliminate air and then filled with coke oven gas to prevent air from leaking back in. Acid absorbent is admitted to the top of the absorber, passes down the column and through the reboiler, and is discharged to the sewer. Steam is passed through the reboiler at the regular operating rate and mixed gases are admitted to the absorber. Steam to the reboiler may be adjusted manually to bring the absorber-rectifier to standard operating conditions as quickly as possible. When the discharge from the reboiler is free of hydrogen sulfide it is assumed that the absorber

has attained operating equilibrium; overhead gases are sent to the acid plant, and the foul solution from the bottom is admitted to the stripper column. Steam is admitted to the stripper at the standard rate and water is passed through the dephlegmator at the maximum cooling rate. This usually provides a dephlegmator discharge at about 40° C. The overhead vapors enter the enriching column, and the reflux ratio is immediately set at 1:1. The initial product contains less than 10% water, and after a few minutes of reflux operation the product has attained the standard strength of 98.5% hydrogen cyanide.

To shut down the unit the mixed gas feed is by-passed to the stack. The stripper remains operating at standard conditions until there is no more overhead discharge. The flow of absorbent through the absorber and into the stripper is continued until all hydrogen cyanide has been removed from the system. If it is necessary to enter any of the process equipment the vessels are filled with the dilute sulfuric acid absorbent, drained, and purged with steam before they are opened. If the plant was to remain idle for a period of several days this procedure would also be followed to prevent polymer formation by residual hydrogen cyanide.

Acid flushing and steam cleaning are used throughout the plant to clean lines and vessels. No alkaline detergents are used at any time.

In the event a pipe that carries hydrogen cyanide must be replaced or repaired, the section of line is isolated and operators in gas masks and rubber gloves loosen the adjacent flange connections until the hydrogen cyanide begins to drip out. A water hose is played on the connection until the dripping stops and then the line is removed.

Vent System

All vents from the hydrogen cyanide recovery unit including those from the relief valves are connected to a 60-foot flare stack. The stack has two separate flares, one for sulfide gases and one for cyanide, with a single ignition system. The sulfide flare is connected to manual vent valves on the inlet knockout and the hydrogen sulfide knockout drums, to a relief valve set for 10 to 12 pounds per square inch on the hydrogen sulfide knockout, and to a 15 pound per square inch relief valve on the absorber reboiler.

The other flare serves manual vents on the cyanide condenser, the reflux weir, the absorber reboiler, the stabilizers, cylinder loading, and meter tanks, all through a vent line catch pot. Most of the vent lines are 4-inch stainless steel although a few are 2 inches. Flame arresters on both flares prevent a blowback into the system. The stabilizer, loading, and meter tanks also have aluminum rupture disks calibrated to release at 10 to 15 pounds per square inch gage. The stabilizers have 8-inch disks; the others use 6-inch. The rupture disks have individual stacks that rise about 10 feet above the vessel.

Auxiliary Equipment

Refrigeration for the plant is provided by two 20-hp. units using Freon refrigerants (10E). The cooling effect is transmitted (3E) to the jacketed pipes and tanks by calcium chloride brine with a specific gravity of 1.2.

All instruments and automatic valves are air operated. The air for this service is taken from the general plant service line and dried in a double tower gas dryer. Each tower contains 65 pounds of silica gel. They operate alternately on 24-hour drying and regenerating cycles. Regeneration is by internal steam coils. The unit has a capacity of 25 cubic feet of air per minute to a dew point of 9° C.

Two banks of three nitrogen cylinders are available to replace the instrument air in case of compressor failure or other casualty. Each cylinder can supply air for the entire instrument system for 6 minutes.

Materials of Construction

Practically all the equipment in the recovery plant which will come in contact with high concentrations of either hydrogen cyanide or hydrogen sulfide is fabricated of Type 304 stainless steel (1E). Although such construction is not absolutely necessary, it prevents discoloration of the product by corrosion products. The sewer that serves the stripper is also of stainless steel since it must handle dilute acid at 100° C. Other sewers are ceramic. Phosphoric acid lines and pumps are of Monel metal.

All process piping is joined by bolted flange joints similar to those commonly used with small soft tubing (9E) (Figure 6). Pipe is flared to a conical shape by special tools on the job. Ease of dismantling and replacing sections of line so connected more than compensate for its relatively high initial cost, according to Koppers' engineers.

High temperature lines are steam traced and magnesia lagged. Glass-wool insulation is used on the brine lines and other pipe carrying streams below atmospheric temperatures. Process vessels have 2 inches of glass wool or 85% magnesia insulation plus a weatherproof asphaltic coating.

Safety Features

The major safety provision of the installation is a system of quick-acting valves that make it possible to drop the contents of any container holding liquid hydrogen cyanide into water almost instantaneously.

The three stabilizer tanks, the meter tank, and the cylinder loading tank are all equipped with 4-inch dump valves that will completely empty them into a 6500-gallon horizontal quench tank in 10 seconds in the event of run-away polymerization. The quench tank is always filled with 4500 gallons of water, enough to quench the contents of all the hydrogen cyanide vessels in the event of trouble. It is equipped with two 420-r.p.m. agitators each with two 16-inch square pitch, horizontal paddles (5E).

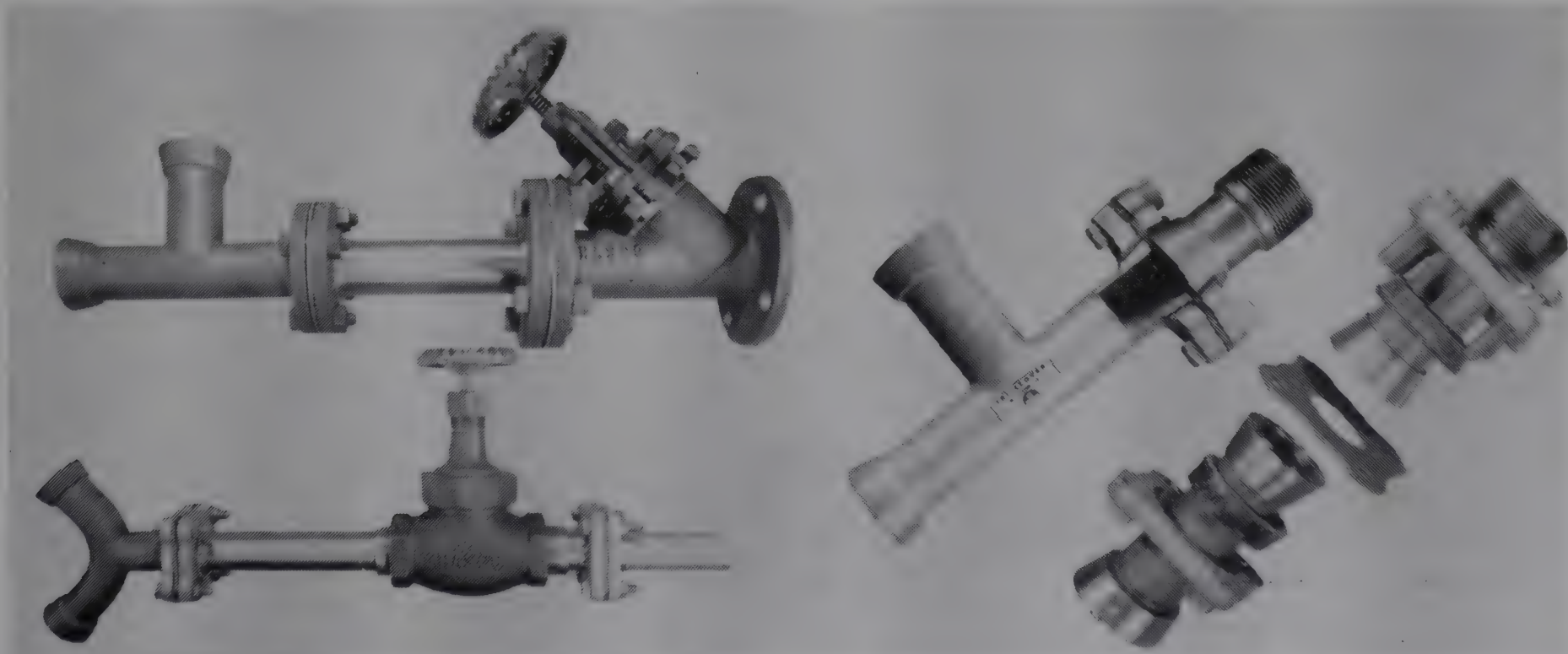


Figure 6. Flanged Conical End Fittings

This precautionary measure has been adopted since the explosion in the initial installation. It has never been necessary to use the quenching system, but if any charge of hydrogen cyanide were quenched in this fashion the contents of the quench tank would be steam stripped in the stripper column and the hydrogen cyanide stripped out would be burned.

The dump valves may be operated manually by individual switches on the control board or they may all be opened simultaneously by a master switch located in the unit's office building. If the temperature in a stabilizer exceeds 10° C. an alarm rings. At 20° C. the valve on that vessel will open automatically. The valves are air operated and controlled by three-way solenoid valves. A standby nitrogen supply is available which will automatically replace the instrument air in case of compressor failure. However, if this standby system fails or the air lines develop a leak that it cannot compensate the valves will open rather than become inoperative in the closed position. Steam valves throughout the plant will automatically close in the event of air pressure failure. In addition to the dump valves the stabilizing tanks are also equipped with 8-inch rupture disks to release the pressure of any explosion or explosive increase in pressure.

As a second major precaution, the plant has been carefully designed to eliminate all pockets where liquid hydrogen cyanide might accumulate. Toward this end, all cyanide-carrying pipes have a minimum slope of 6 inches in every 10 feet. Sharp bends in piping or any other construction that might induce eddies in the flow of liquid hydrogen cyanide have also been avoided.

In addition to the polymer explosion hazard, hydrogen cyanide is also combustible, explosive in the usual sense, and, of course, poisonous. It has an ignition temperature of 585° C. and is explosive in concentrations between 11 and 60% (22). It has a toxic limit of 50 p.p.m. and may be absorbed through the skin. Although as a gas it is lighter than air and has a low persistence, it is a liquid below 26° C. and as such will persist for long periods.

Koppers' safety engineers recommend water as the best fire extinguisher for hydrogen cyanide since it will dissolve the material as well as cool it. A manually-triggered sprinkler system fed from a 75,000-gallon tank protects the stabilizer tanks. A dike around these vessels will contain a major spill for added protection.

The toxicity hazard has been beaten by rigid enforcement of regulations regarding the use of gas masks and rubber gloves and especially close attention to the prevention of skin absorption from contaminated clothing. All handling of hydrogen cyanide, even in small sample quantities, must be done within sight of another man. Safety showers and eyewash fountains have been provided generously.

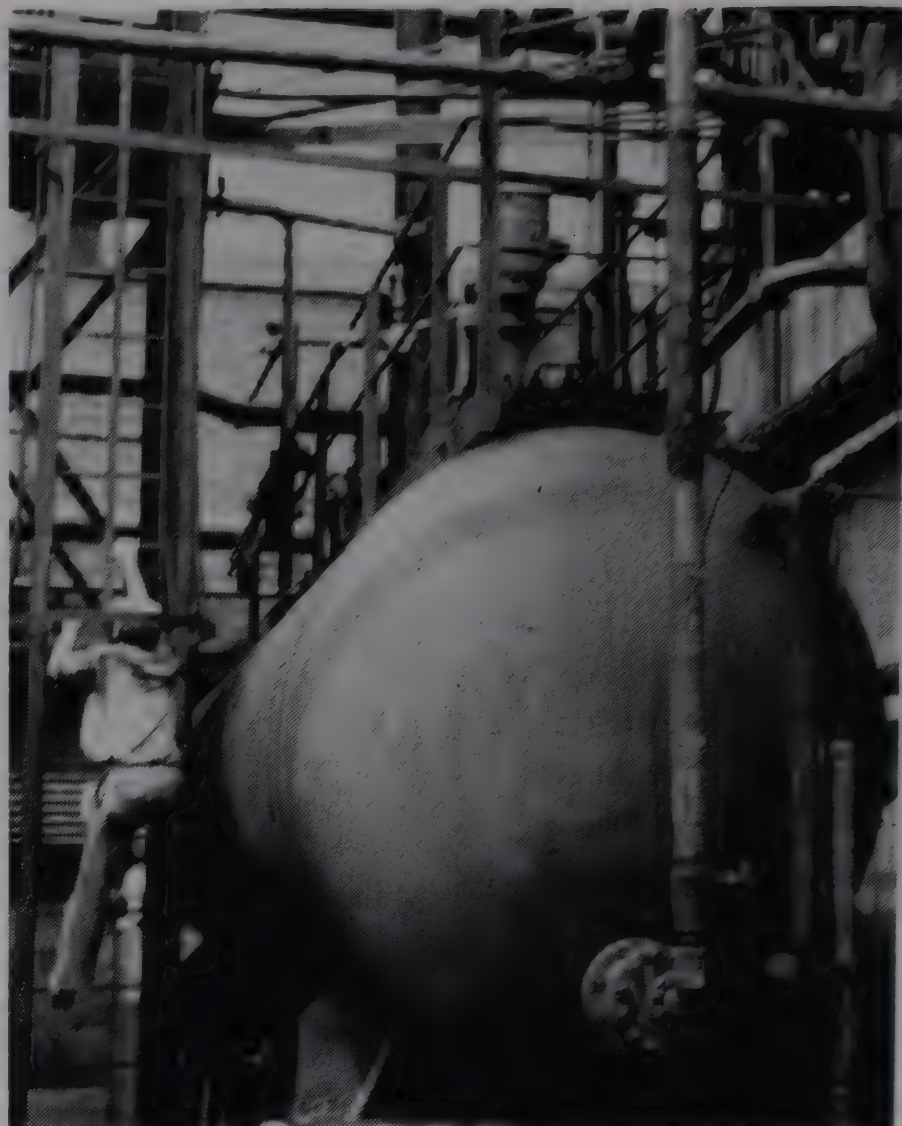
The hydrogen sulfide provides its share of headaches also. It is explosive when present in the air from 4 to 46%, and it will ignite at about 350° C. Furthermore, its toxic limit in the atmosphere is even lower than that of hydrogen cyanide, although its strong odor makes it easier to detect. However, the hydrogen sulfide is handled very little once it is isolated from the mixed gas; it goes directly to the sulfur burner and, consequently, does not introduce as widespread a hazard as the cyanide.

A monthly inspection of all vessels and lines is made to detect structural weaknesses and accumulations of polymer. Checks with cyanide test paper and then an actual gas analysis are made before anyone enters a process vessel.

Chemical Control

Most chemical analyses on the recovery process are run once a day. The mixed gas feed to the hydrogen cyanide absorber is assayed for hydrogen sulfide, hydrogen cyanide, carbon dioxide, and ammonia. The gas going to the sulfuric acid plant is checked for hydrogen cyanide and carbon dioxide. The stripping column feed is analyzed for hydrogen sulfide and hydrogen cyanide, and hydrogen cyanide is run on the stripper bottoms.

While hydrogen cyanide is being run into a stabilizer the tank



Quench Tank

Any vessel containing HCN can be dumped into this 6500-gallon water tank in 10 seconds

is checked hourly for cyanide concentration by specific gravity and acid content by titration. If a charge is allowed to stay in the stabilizer for an extended period it is checked for acid stabilizer content once during each shift.

After a stabilizer tank has been filled it is sampled for specific gravity, hydrogen cyanide, total inhibitor content (base titration), phosphoric acid, sulfuric acid, sulfur dioxide, hydrogen sulfide, color, noncondensables, and a standard stability test involving color change after addition of ammonium hydroxide.

POTENTIAL OF THE PROCESS

The coke oven installation of the Koppers Co. at Kearny is a small one as coke oven batteries go these days. Some of the plants associated with steel mills process several times the coke handled at Kearny. However, the Kearny operation is large enough to afford typical operation conditions for a study of the hydrogen cyanide-hydrogen sulfide recovery system. The operating history now available indicates that the recovery operation will be economical. For simple hydrogen sulfide recovery it must compete with a number of other systems. However, that phase of the operation has been available as the "vacuum carbonate purification process" for some time and has proved its competitive position. Its adaptability to cyanide recovery now gives it an added advantage. It is obvious from the much-lamented current state of sulfur supplies that sulfur recovery from hydrocarbon gases will enjoy increasing importance in the years to come.

The present stimulation of the market for cyanides caused by the introduction of acrylonitrile fibers promises the hydrogen cyanide recovery operation a strong market for its product. The new cyanide plants springing up throughout the country give ample evidence that the chemical industry is expecting a boom in the demand for cyanide.

Although the use of cyanide in the form of a 30% sodium cyanide solution is unfamiliar to most consumers, Koppers' marketing



Chemical Analysis Equipment

Equipment adjacent to receiving tanks permits frequent and quick determinations of stabilizer in liquid HCN

experience to date indicates that enough cyanide applications can be modified to use this form of the material to absorb all potential production from coke oven gases. Pittsburgh Coke and Chemical Co. has had little trouble disposing of the solutions they have produced for the past 9 years to large unit consumers within short hauling distance of their plant. Similarly, Koppers has found a ready market for their high purity solutions, particularly among manufacturers of dyestuff intermediates and other fine chemicals. Of course there are some cyanide markets—such as the heat treating of steel which now represents the major single market for sodium cyanide and the recovery of precious metals—in which the cyanide solutions can never compete. Some of the solution has been sold to the plating industry.

It is not yet apparent whether the solution will be suitable for use in the production of acrylonitrile or adiponitrile for synthetic fiber; however, as fiber production absorbs large portions of the primary hydrogen and sodium cyanide supply, the sodium cyanide solutions should find ample applications as a replacement.

The solutions enjoy certain positive advantages, primarily in handling, over both gaseous hydrogen cyanide and solid sodium cyanide. The solutions do not present as serious a toxicity hazard as the gas and are much more easily assayed, measured, and metered than the solid. Furthermore, they can be shipped to the consumer and transferred within the plant with greater ease and less danger.

The gross economics of this process, like that of any by-product recovery, are exceedingly difficult to calculate. In most gas-producing operations it is essential that hydrogen sulfide be removed from the product either to avoid air pollution or corrosion of pipes and tanks or in the case of open-hearth operations to

avoid sulfur contamination of the furnace charge. Hydrogen cyanide effluents, either as a gas or in solution, also present a pollution problem although their concentration is usually low enough to avoid being a public nuisance. Both of these gases are highly corrosive and gas plant operators say that their presence in the air at the plant site increases measurably the rate of external corrosion or surface coating failure.

The benefits derived from the elimination of hydrogen sulfide and hydrogen cyanide as plant effluents are at best intangible. Their value will vary with the atmospheric conditions around a given plant and with the pollution control regulations under which it must operate. However, preliminary calculations from the Kearny experience indicate that even disregarding these intangible benefits, the hydrogen sulfide and hydrogen cyanide recovery system should pay for its operation and amortize its initial cost within a reasonable plant life at the present market prices for the recovered materials. Should increased demand raise these prices or should regulations demand that these gases be removed from the plant effluents the operation will offer a definite economic advantage.

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Processing Equipment

- (1E) American Iron & Steel Institute, New York, N. Y., (ASTM A167-44, Grade 3), C = 0.20%; Mn = 2% max.; P = 0.035% max.; S = 0.030% max.; Si = 1.0% max.; C₁ = 18-22%; Ni = 8-11%.
- (2E) Fischer & Porter Co., Hatboro, Pa., Rotaweir flow proportioner.
- (3E) Harris Pump and Supply, Greenville, S. C., 1-inch, DS6-2, Dayton Dowd type.
- (4E) Heresite and Chemical, Inc., Manitowoc, Wis., Herecol.
- (5E) Industrial Process Engineers, Newark, N. J., gear motor drive type.
- (6E) Ingersoll-Rand, New York, N. Y., Cameron No. 1 Class MCS, single-stage pump.
- (7E) Lapp Insulator Co., Inc., LeRoy, N. Y., Lapp Pulsofeeder CPS-1, piston type, Monel.
- (8E) Tabor Pump Co., Buffalo, N. Y., Vertical Type No. C-2, 1-hp. sump pump.
- (9E) Tri-Clover Manufacturing Co., Kenosha, Wis., Tri-Clover pipe connections.
- (10E) York Corporation, York, Pa., 363W York 20-hp. refrigeration units.

PIONEER SURFACTANT

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in collaboration with

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General Aniline & Film Corporation,
Grasselli, N. J.

Igepon T at Gelling Point
Just Before Discharge of Kettle Batch

THE American housewife who is being rapidly educated to the use of something other than soap in her dishpan and washing machine is probably inclined to think that some wonderful chemist has been sitting up nights thinking of a way to lighten her daily routine. Anyone listening to the daytime radio will certainly understand how she has been led to that conclusion. However, milady is misinformed. The consumer packaged powders and liquids which now account for the great majority of the "synthetic" detergents produced are actually the incidental result of an attempt to meet the long-standing requirement of the textile industry for a surface-active agent which would be effective under the conditions of acidity and hard water encountered in textile processing. The first feeble attempt to meet this need was sulfated castor oil or turkey red oil named for the turkey red dye bath in which it is used.

Turkey red oil was the only contender in the field for almost a hundred years but in the 1920's German manufacturers of synthetic organics began a concentrated search for a substitute for soap or a "universal soap." The first result of this search was the development of Nekal, an alkyl naphthalene sulfonate. This type compound found application as a wetting agent, but it had almost no detergent value. The quest took a big step forward when Bertsch (1) localized the cause of most of the shortcomings of conventional soap in the active carboxyl group. From this

point of common departure H. T. Böhme, A.-G., and I. G. Farbenindustrie took the lead in attempting to block the troublesome group (3, 10). Böhme produced the first group of commercial products—the Avirol series, sulfuric acid esters of butyl ricinoleic esters, in 1928 (8). Two years later they introduced a series of fatty alcohol sulfates under the trade name of Gardinol (2, 8, 15). These compounds were made by sulfating fatty alcohols obtained by the high pressure hydrogenation of fatty acids (12).

During the same period, I. G. Farbenindustrie, taking a different approach to the problem, concentrated their investigations on esters of fatty acids. In 1930 they marketed in Germany the Igepon A series which comprised fatty acid esters of hydroxyethanesulfonic acid (4, 8, 13). The "A" in the name derives from *äthan*, the German spelling of ethane. The A-type Igepon is an ester; it proved to be too unstable for many applications, and in 1931 I. G. Farbenindustrie submitted the Igepon T series to the German market (8, 13). These products represent still another approach to the elimination of the carboxyl group. They are amides—derivatives of taurine which gives the group its type name—and are sufficiently stable for most textile processing work except the carbonizing of wool where a strong sulfuric acid bath is encountered.

Surprisingly enough, these pioneer surfactants are still on the

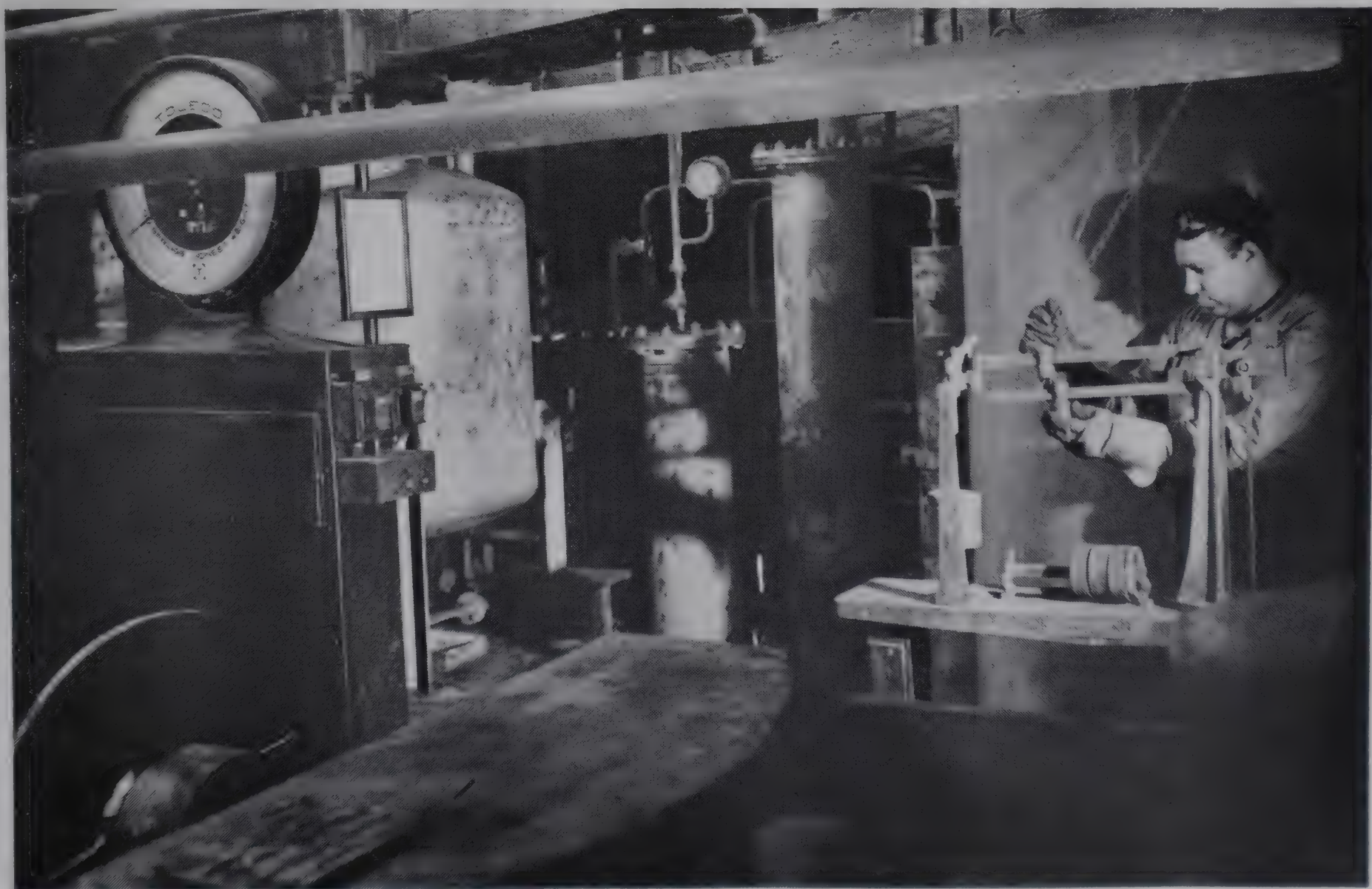
market in essentially their original form. Avirol is still made by Böhme in Europe. Gardinol in the United States has become Duponol on the Du Pont label and Orvus and Dreft when made by Procter and Gamble. Igepon A types are still made by General Aniline & Film, although it was originally thought that they would be replaced entirely by the compounds of the T series. Igepon T has enjoyed a steady expansion of market up to the present time in spite of the advent of the alkyl benzene sulfonates (Santomer, Ultrawet, and Oronite) resulting from American extension of the German work on the alkyl naphthalene sulfonates, which produced the first cyclic-derived detergent, Nacconol, introduced in 1933 by National Aniline and Chemical Company.

The migration of the synthetic detergents to the United States is in itself an interesting story (5). The first immigrant to arrive was Gardinol, presented under the sponsorship of National Aniline in 1930, the same year that it was introduced in Europe (7, 8, 15). National Aniline offered the German product under a marketing agreement with Böhme. However, in 1932 Du Pont and Procter and Gamble became interested in the fatty alcohol sulfates and subsequently manufactured and sold them in this country, while National Aniline concentrated its efforts on the development of its own Nacconol products. In the textile field, the fatty alcohol sulfates were marketed under the trade name Gardinol by the Gardinol Corporation (controlled by Du Pont and Procter and Gamble) until 1946 when it was dissolved and went out of business. Both Du Pont and Procter and Gamble are still making and selling the fatty alcohol sulfates under their respective trade names under license from American Hyalsol Corporation, the capital stock of which was vested in the Alien Property Custodian. Other manufacturers have also taken licenses from American Hyalsol Company.

The Igepon-type surfactants immigrated in a simpler fashion. When the series was first developed, I. G. Farbenindustrie transmitted the production details to their American subsidiary, General Aniline Works, Incorporated, and suggested that they consider producing the materials in this country if they thought the potential market warranted it.

Production of Igepon A was begun at the General Aniline plant at Linden, N. J., in 1931, and the following year Igepon T was produced at the same site. All the Igepon products made in this country since that time have been made at this same plant with the exception of a small wartime production at the company's Rensselaer, N. Y., plant. Aside from the basic technology, the American production technique for these compounds has been developed independently of the German practice. I. G. Farbenindustrie had made less than 80,000 pounds of Igepon T in Germany when the first production came out of the Linden plant. In fact T gel, the largest selling Igepon in this country, has never been made in Germany. It was developed entirely at Linden and was first produced there in 1933. Its popularity reflects the textile industry's preference for an easy-to-handle dustless product. In 1940 I. G. Farbenindustrie sold the American rights to the patents covering the manufacture of Igepon (6) and several other compounds to General Aniline.

Shortly after the acquisition of the patents by General Aniline the United States declared war on Germany and the foreign-owned stock of the company was confiscated by the Alien Property Custodian (14). Since the end of the war the federal government has disposed of most of the equities acquired under this act. However, General Aniline remains under government management because of a court action brought by a Swiss corporation which claims to be the majority stockholder. They claim that because their incorporation is in a country which was never



Weigh Tanks for Oleic Acid and Phosphorus Trichloride Used in Production of Oleic Acid Chloride

Air filtering and drying system cylinders are shown in background

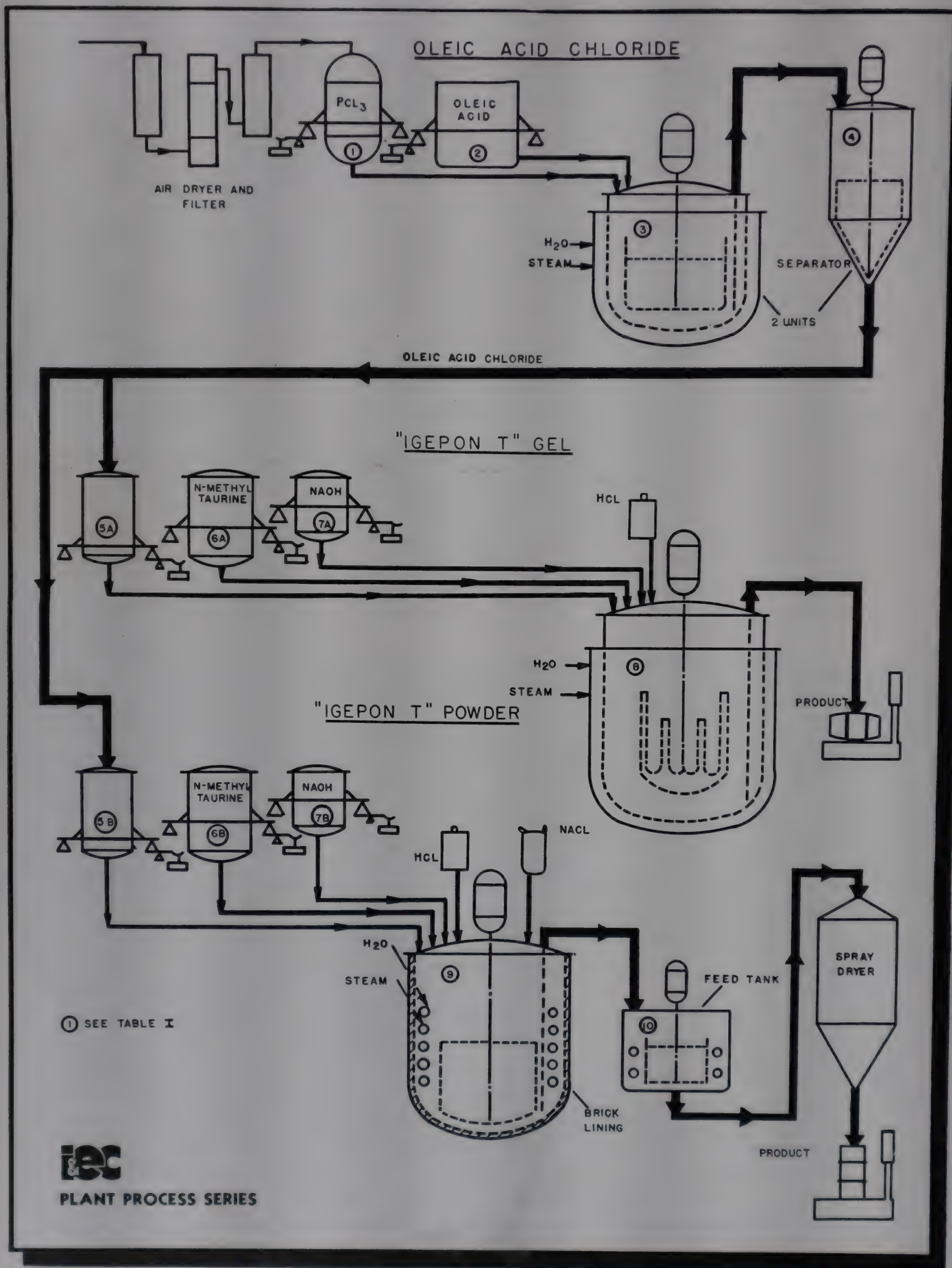


Figure 1. Flow Sheet for Production of Igepon T at Linden, N. J., Plant of General Aniline & Film Corporation

TABLE I. PROCESS VESSELS

Key to Figure 1	Name	Capacity, Gallons	Vessel Walls		Temperature Control	Agitation	
			Material	Lining		Kind	Power, hp.
1	PCl ₃ weigh tank (5000-lb. scale)	185	Carbon steel	1/4-inch homogeneous lead-lined
2	Oleic acid weigh-tank	600	Carbon steel	10
3	Acid chloride kettle	750	Carbon steel	1/8-inch homogeneous lead-lined	Steam and cooling water jacketed	Lead covered horseshoe	10
4	Acid chloride cone tank	1500	Carbon steel	1/4-inch homogeneous lead-lined	1 1/2-inch lead steam coils around outside of lower cone	Lead covered blade	1.5 3
5a	Acid chloride weigh tank (6000-lb. scale)	250	Carbon steel	1/4-inch homogeneous lead-lined
5b	Acid chloride weigh tank (6000-lb. scale)	564	Carbon steel	1/4-inch homogeneous lead-lined
6a	Methyltaurine weigh tank (6000-lb. scale)	766	Carbon steel
6b	Methyltaurine weigh tank (6000-lb. scale)	766	Carbon steel
7a	NaOH weigh tank (4000-lb. scale)	200	Carbon steel
7b	NaOH weigh tank (4000-lb. scale)	250	Carbon steel
8	Auxiliary kettle	3000	Stainless steel	Steam and cooling water jacketed	Stainless steel anchor	25 12.5
9	Condensation kettle	3000	Carbon steel	Brick	1.5-inch stainless steel submerged coils steam or cooling water	Stainless steel four-fingered gate	25
10	Spray dryer feed tank	6800	Carbon steel	Loose lead-lined	Five turns, 2-inch lead submerged coil for steam	Wooden gate	5

at war with the United States their property has been confiscated illegally. The federal government contends that the Swiss company is only a dummy for the German I. G. Farbenindustrie. Until these claims have either been confirmed or denied the United States cannot obtain a clear title to the company and so cannot dispose of it. General Aniline preserves the conventional organizational form of a private industry with the United States government as almost its only stockholder.

LINDEN, N. J., PLANT

General Aniline's Linden plant is known officially as the Grasselli Plant because it was originally part of the Grasselli Chemical Company installation for the production of aniline dyestuffs and heavy chemicals. In 1924 I. G. Farbenindustrie, seeing the growth of the American chemical industry behind increasing protective tariffs and wishing to get back into the American market from the inside, formed a joint company with Grasselli Chemical Company. The new company, Grasselli Dyestuff Corporation, acquired the entire dyestuff business and manufacturing facilities of the Grasselli Chemical Company. Consequently the Grasselli Chemical Company's Linden plant was literally split down the middle. The heavy chemicals half of the installation was retained by Grasselli Chemical Company and the dye works became the property of the new Grasselli Dyestuff Corporation. When, in 1928, Du Pont bought out the Grasselli Chemical Company, it did not assume that company's interest in the dyestuff company. I. G. Farbenindustrie was the logical purchaser of this interest and assumed full ownership of Grasselli Dyestuffs. Shortly after this acquisition I. G. Farbenindustrie changed the name of the company to General Aniline Works, Incorporated. In 1939, shortly before the transfer of ownership of the company from the German I. G. to Swiss I. G., the name was changed again to its present form—General Aniline & Film Corporation.

CHEMISTRY OF IGEPON T

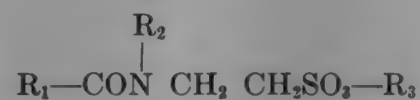
The American patent which covers the manufacture of Igepon is particularly interesting in that it potentially applies to an almost unbelievable number of compounds (8). In essence it specifies a compound of the type:



R₁, R₂, and R₃ are branched or straight aliphatic, cycloaliphatic, or aromatic hydrocarbon groups, and may even include

heterocyclic rings. It is further assumed that at least one solubilizing sulfonic or sulfuric acid ester group is attached to one of the R's. One or two of the R's may be hydrogen provided the total carbons in all three R's are not less than eight. If the R's are limited to a maximum of twenty carbons it is certainly not difficult to imagine thirty different hydrocarbon configurations at any of these positions. This would permit $30 \times 30 \times 30 = 27,000$ various structures based on carbon arrangements alone. Since a sulfonic or a sulfuric acid ester group will be substituted on one or more of the R's and these groups may exist as free acids, metallic salts, or organic-base salts, we may assume ten variables for the various metal salts and the free acids, and at least six for the substitution and have $27,000 \times 6 \times 10 = 1,620,000$ variations. The General Aniline & Film Corporation has prepared about 200 of these compounds which certainly leaves a vast number of potentially valuable surfactants among the still unexplored Igepon-type compounds.

If we restrict our considerations to the commonly accepted essence of the patent—namely, acyl alkyl taurates—represented by the structural scheme,



there are fewer possibilities. R₁ then represents hydrocarbon radicals of the fatty acid series. For economic reasons, it is probable that the number of carbons in R₁ will be between twelve and eighteen. R₂ represents an alkyl or cycloaliphatic group which should range from one to eight carbons. Total carbons in R₁ and R₂ preferably should be not less than twelve nor more than twenty-one. Beyond these limits the quality of the product falls off sharply in one of several properties. R₃ may be a metal or an organic base or hydrogen. A computation of the number of possible products under the above-stated limits might reach 1000.

The effect of changes in structure are fairly well defined. Little detergency is obtained unless R₁ and R₂ combined contain at least twelve carbon atoms. Detergency is increased by increasing the length of either R₁ or R₂ or both. The limit is reached at approximately sixteen carbon atoms for R₁ if the chain is straight and saturated. If unsaturated, then maximum detergency occurs at approximately eighteen carbons, and it is believed that with more unsaturation the maximum length of carbons is further increased. Departures from straight chain in R₁, by branching or by introduction of a solubilizing group, will decrease detergency but increase the wetting power. A

Minor changes in procedure yield products of various concentrations and physical states.

The gel accounts for most of the production. This product is made in a brick-lined kettle equipped with a four-fingered stainless steel agitator. A stainless steel submerged coil provides temperature control. The kettle has stainless steel feed lines for oleic acid chloride and muriatic acid and caustic solution, a stainless steel thermometer well, and a lead vent pipe. Air for forcing the charge out of the kettle is introduced into the vent pipe.

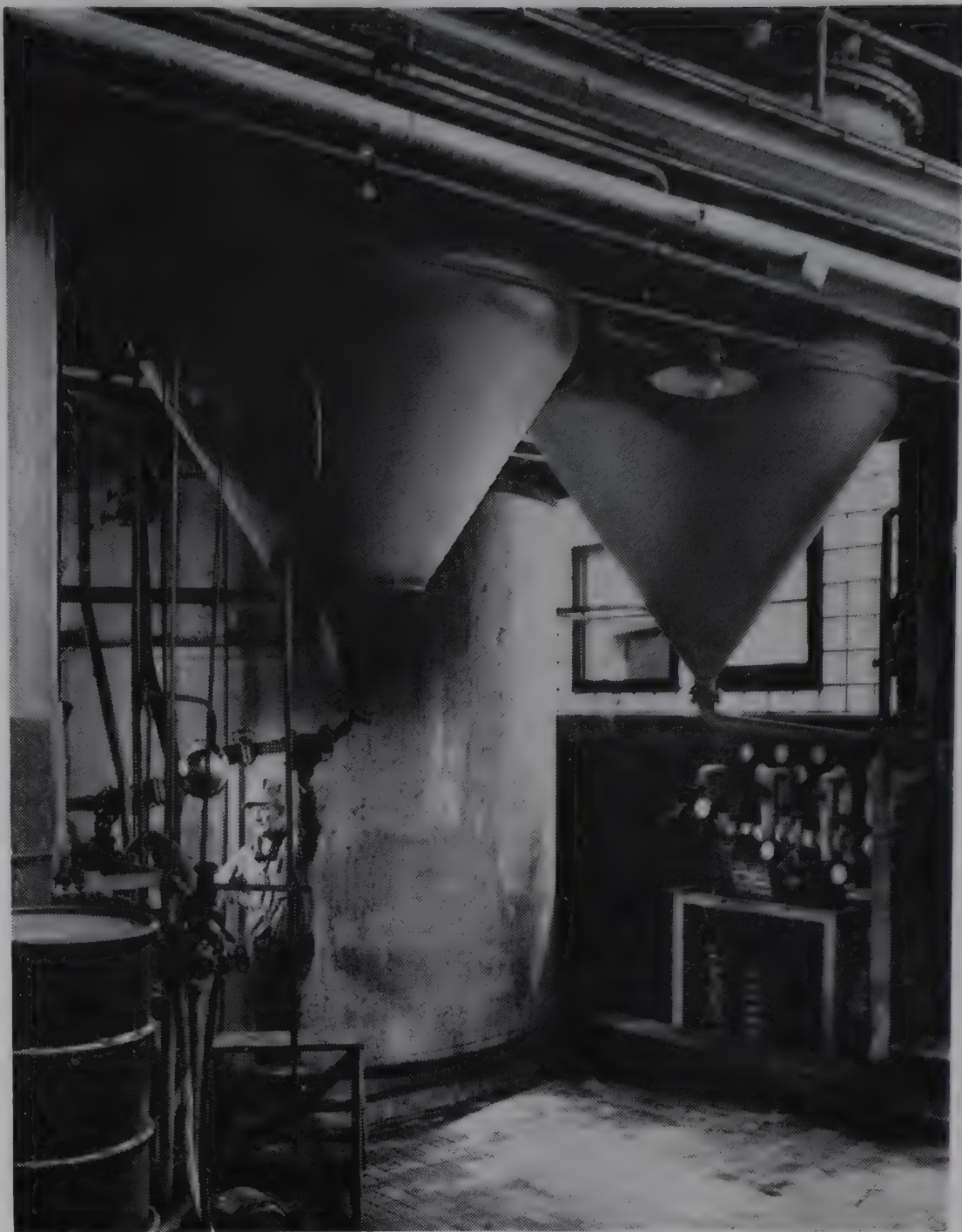
A stainless steel kettle, equipped with an anchor-type agitator is also available. Process temperatures in this kettle are controlled by a steel jacket connected to both steam and cooling water lines. Inlets and vents are arranged similarly to those in the larger kettle.

To begin the batch 25 to 30% aqueous solution of *N*-methyltaurine is blown over from the storage tanks until an amount of solution equal to 875 pounds of *N*-methyltaurine has entered the weigh tank. The correct gross weight of this charge, based on the *N*-methyltaurine analysis of the storage tank, is supplied to the operator by the analytical laboratory. This charge is then dropped by gravity into the reaction kettle, and the flow of cooling water is started in the jacket to bring the temperature of the charge down to 22° to 25° C. Water weighed in the same weigh tank is then added to bring the total weight of the charge at that point to 12,000 pounds. Addition of 30% aqueous caustic solution is begun and when the equivalent of 140 pounds of sodium hydroxide has been weighed in, oleic acid chloride is introduced from a lead-lined weigh tank. The caustic and acid chloride enter the kettle through separate perforated stainless steel pipes below the level of the initial taurine charge. This practice minimizes the liberation of noxious fumes, reduces the corrosive effect of the acid chloride above the liquid level, and safeguards against side reaction between sodium hydroxide and oleic acid chloride. Simultaneous addition of the two reactants is continued for 4 to 6 hours until a total of 425 pounds of sodium hydroxide and 2100 pounds of about 92% oleic acid chloride have been charged. The rate of addition of these two solutions is adjusted to maintain a slight stoichiometric excess of sodium hydroxide in the kettle at all times, as determined by spot tests on triazene paper—2-(4-nitro-*O*-tolyl diazoamino)-4-sulfobenzoic acid.

After all the reagents have been added the charge is agitated for an additional hour to ensure completion of the reaction. Cooling water is circulated through the coils at maximum flow rate during the entire reaction period. During the winter months the charge is about 22° C. at the beginning of the reaction and rises to 27° C. However, in the summertime the final temperature may go as high as 40° C.

After the reaction has been completed a sample is taken and the percentage of excess *N*-methyltaurine is determined by coupling with diazotized *m*-nitraniline. It is desirable to have a slight excess of *N*-methyltaurine in the product to ensure that the reaction has gone to completion.

After completion of the reaction muriatic acid is added to the kettle through a glass and rubber siphon from a 12-gallon carboy mounted on a 200-pound platform scale. The entire scale assembly is elevated by a windlass device to control the acid flow through the siphon (4E). Acid is added until the charge gives a



Oleic Acid Chloride and Waste Phosphorous Acid Are Separated in Cone Tanks

Heating coils and steam tracing can be seen on the tank being discharged by the operator; these have been removed from the tank on the right

slightly red spot test with brilliant-yellow paper (pH 6 to 8). This neutralization usually requires about 150 pounds of acid. In making some of the special Igepon products additional muriatic acid is added at this point.

In making the standard T gel the neutralized batch is diluted to 17,000 pounds with water and 7 pounds of a light, floral, liquid perfume. The charge is then heated to 55° C. and held there for 1.5 hours.

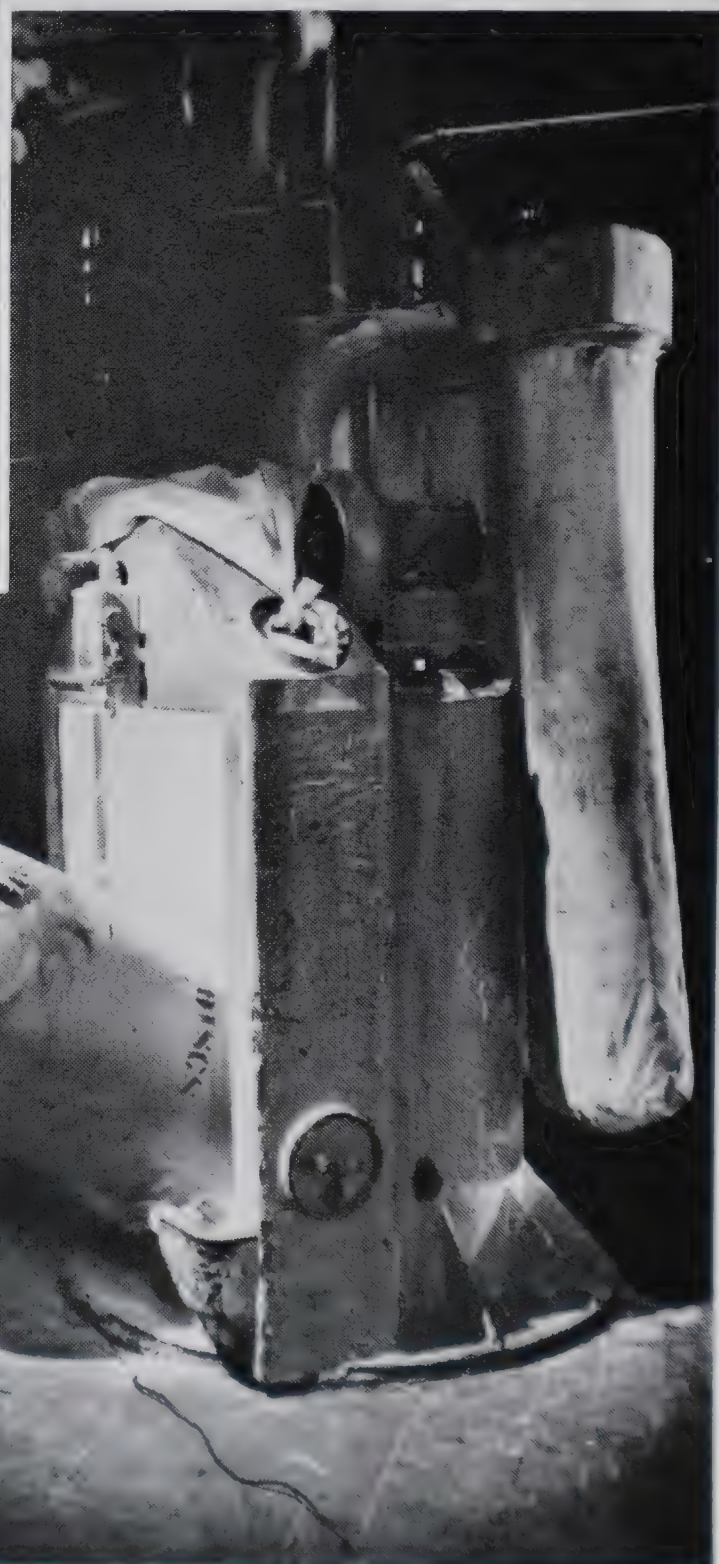
The charge is blown into white oak, gum, or ashwood barrels. Air used to blow out the batch passes through a trap to remove rust particles which would tend to darken the finished product. As a further precaution against contamination a 0.007-inch opening stainless steel filter on the product discharge line removes all solid particles from the liquid product before it enters the shipping containers. The barrels are allowed to cool on the shipping platform, and when the Igepon reaches a temperature of about 40° C. it sets up as a firm, opalescent gel.

Recently several experimental shipments of Igepon T gel have been made in polyethylene-lined, fiberboard drums. Although these drums are more expensive than the wooden barrels they are easier to fill and to handle. Consequently, it costs only about \$4 to pack 50 gallons of gel in the fiber drum compared to \$6 for 55 gallons in a barrel. If further evaluation confirms the superiority of these containers they may supplant wooden barrels for shipment of Igepon T gel.



←
**German-Built Spray Dryer Used
on Igepon T Powder**

Dryer is slightly more complex than ones designed in this country; main chamber is shown in background; primary and secondary cyclone separators in foreground; on far right is tank in which final exhaust is water-scrubbed



→
**Igepon T Powder is Transferred in
Drums from Spray Dryer to Hooded
Mill**

Material is packaged for shipment directly
from discharge of the mill

The batch of gel yields about 107,00 pounds, having a composition of 15.3 to 16.3% oleoylmethyltaurine [sodium *N*-(9-octadecenoyl)-*N*-methyltaurate], 0.8 to 1.0% sodium oleate, 0.14% *N*-methyltaurine, 4.0% sodium chloride, and 78% water. This represents approximately the theoretical yield.

Igepon T Powder. The second most important Igepon T product is the standard powder. In manufacturing this product the initial charge of 30% *N*-methyltaurine solution contains 930 pounds of 100% *N*-methyltaurine, and when diluted with water to 12,000 pounds it gives a slightly more concentrated solution than that used in the gel process. As a 30% solution 172 pounds of sodium hydroxide are added to this initial charge to keep the reaction mixture on the alkaline side. Then 2220 pounds of technical oleic acid chloride are added simultaneously with 295 pounds of sodium hydroxide as a 30% solution over a period of 4 to 6 hours, as in the gel production.

The batch is stirred for 1 hour after charging is completed and any excess *N*-methyltaurine is reacted with additional acid chloride and caustic soda as in the production of gel. The completely reacted charge is then heated to 50° C. by the steam coils and neutralized to the brilliant-yellow end point with muriatic acid. Immediately after neutralization 5200 pounds of common salt are dumped into the batch from bags, and water is added to bring the total weight of the batch to about 26,000 pounds. At this concentration, about 36% solids, the salt is completely dissolved. It is important that no suspended solid material remains in the charge because it would plug up the nozzles of the spray dryer. If the pH of the batch after the addition of the salt does not fall between 7.1 and 7.3, sodium hydroxide or muriatic acid is added to adjust the pH within these limits.

The salt-loaded mixture is blown from the reaction kettles into a $\frac{3}{8}$ -inch lead-lined steel feed tank. The charge is heated to 50° C. by lead steam coils in the feed tank and then is pumped to the three 10-gallon feed pots of the spray dryer (Figure 2).

The dryer atomizers use air at 80 pounds per square inch pressure heated to 220° to 225° C. by a steam coil heat exchanger. The relatively high feed pressure is necessary to maintain 50 pounds pressure at the injection nozzles to ensure adequate atomization in the tower. Air supplied to top of the dryer is preheated to about 225° C. by an oil-fired furnace and forced into the dryer by a centrifugal fan at a rate of about 250 cubic feet per minute. The major part of the dried powder is discharged from the bottom of the dryer tower and carried along by the added cold air into the primary cyclone separator from which it drops directly into a transfer drum. About 10% of the product, however, is carried through the cyclone and is reintroduced into the dryer chamber. A second take-off from the dryer chamber is located just above the bottom taper. This duct carries a more dilute stream of air-borne powder into a larger, secondary cyclone separator. The solids which fall out in this separator are refluidized by more cold air and returned to the top of the primary cyclone. The overhead from the secondary cyclone, containing 7 to 10% of the product, is introduced into a water scrubber. One water spray above the inlet and three below remove all but about 2% of the product from the dryer exhaust. The scrubbed air is vented to the atmosphere. The liquor is drawn from the bottom of the tower into a storage tank. Make-up water is added to this tank by an automatic level



Condensation Kettle and Oleic Acid Chloride and Methyltaurine Weigh Tanks

Operator is checking the batch for alkalinity with indicator paper

control. A high-silicon iron pump (1E), drawing from the tank, recycles water to the spray nozzles and supplies process water to the condensation kettle.

If a kettle batch is made each day the dryer feed pots can be kept full and provide an uninterrupted feed to the dryer. Under these circumstances the dryer can handle as much as 360 to 400 pounds of Igepon per hour, as it has a rated capacity of 770 pounds of water per hour.

The product comes from the dryer as low density granules which are lightly milled in a paddle mixer to break up the larger lumps and to mix in 500 grams of a light floral perfume per ton of Igepon. From the mill the powder is dropped directly into the open-top steel drums in which it will be shipped.

Yields of powdered product run around 8200 pounds per batch and analyze about 30.5 to 32.5% oleoylmethyltaurine, 1.5 to 3.0% sodium oleate, and 0.14 to 0.8% *N*-methyltaurine; the remainder of the powder comprises inorganic salts. Chief among these is sodium chloride and a trace of sodium sulfate. However, phosphite salts (about 3%) are also present; these are formed from the excess phosphorus trichloride dissolved in the oleic acid chloride. The yield is about 91% of theoretical.

RAW MATERIALS

Oleic acid for the production of oleic acid chloride is delivered either in steel tank cars or tank trucks from which it is blown by air pressure to a 9000-gallon steel storage tank inside the production building. The tank is made of 0.5-inch welded plates. A feed tank is filled from the storage tank by gravity; it holds 550

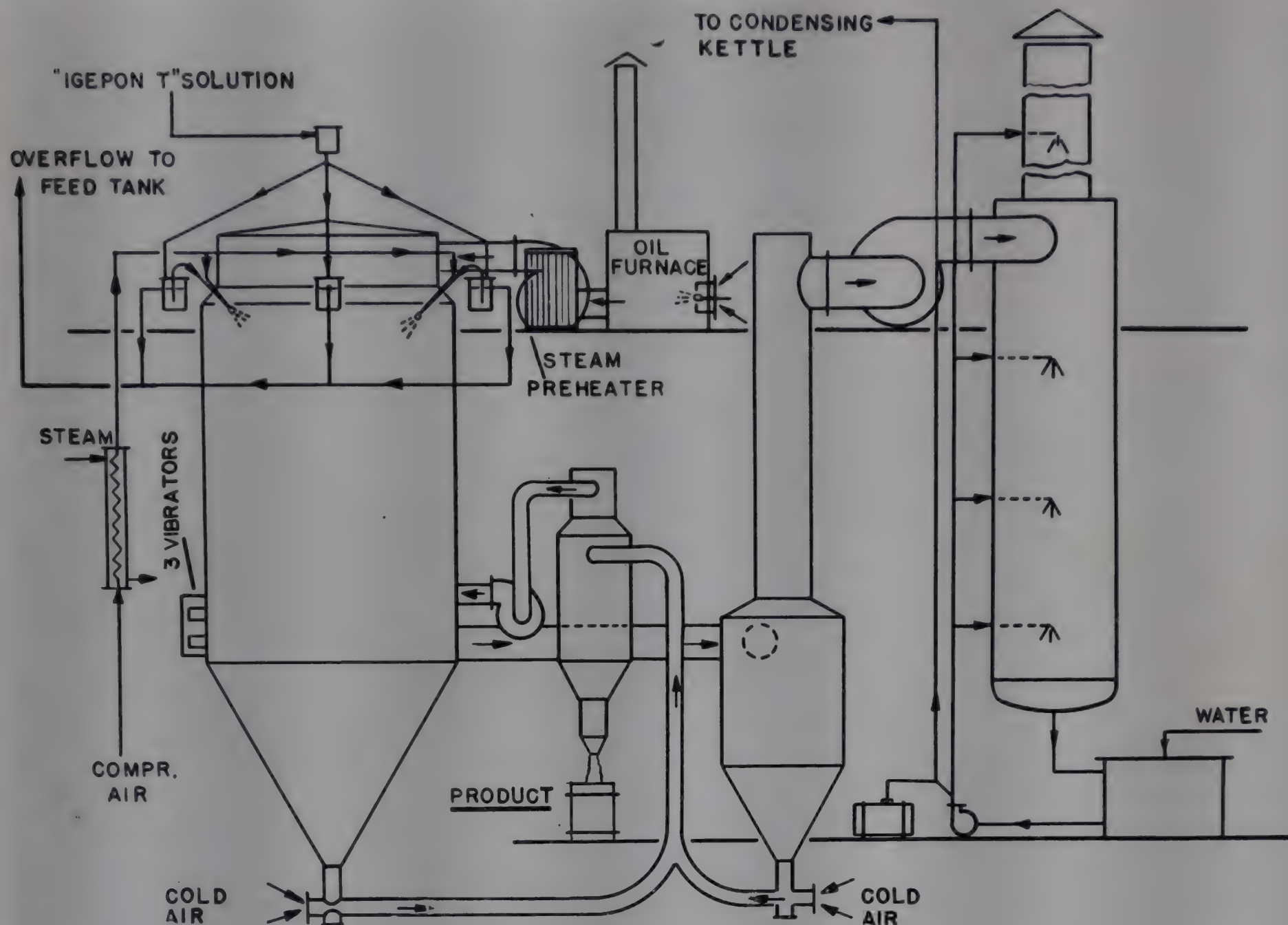


Figure 2. Spray Dryer

gallons and is built of 0.5-inch carbon steel. This tank is of more recent construction and is tested to withstand 45 pounds per square inch pressure so that the transfer of oleic acid from it to the weigh tanks can be made by blowing with air. This intermediate tank eliminates the necessity of subjecting the main storage tank to the pressure required for pneumatic transfer.

It is extremely important that a high quality of oleic acid be used in this process. If an excessive amount of esters or unsaponifiable material is present the resultant Igepon will have an excess of free fat which tends to make the gels cloudy.

General Aniline's acceptance specifications for oleic acid are as follows:

Titer, ° C.	4-6
Cloud point, ° C.	3.3-6.7
Color (Lovibond 1-inch Column Red)	5-8
Saponification No.	196-199
Acid No.	195-198
Iodine No.	90-93
Free fatty acid (as oleic), %	98-99.5
Unsaponifiables, %	2.0-3.5

Phosphorus trichloride is obtained by lead-lined tank car. Cars are unloaded by air pressure into a 6100-gallon homogeneously lead-lined storage tank located outside the operating buildings for safety reasons. This tank of 0.5-inch carbon steel is fitted with a 2-inch lead vent and a lead line connecting it to a weigh tank of similar construction. Phosphorus trichloride is held to the following specifications:

Color	Water white
Turbidity	None
Assay (PCl ₃)	99.5%
Distillation range	First 99%, 74.5-78.0° C
Free P ₂	None
Distillation residue	0.5%

The *N*-methyltaurine used in the Igepon T condensation reaction is manufactured by the intermediates department of the General Aniline Works at Linden (9). It is delivered as a 25 to 30% filtered aqueous solution to the Igepon T area by a 2700-gallon steel tank trailer.

The 30 and 50% caustic soda solutions and the muriatic acid used to control the pH of the batch at various points in the processes are obtained as standard commercial products from various suppliers. These are usually delivered to the plant in tank cars although they may be received in tank trucks. Both the acid and alkali are stored in central storage tanks that serve other processes in the works besides the Igepon T operations. The alkali is piped to intermediate storage tanks in the Igepon area. The acid, which is used in relatively small quantities, is drawn off into 12-gallon carboys which are trucked to the Igepon kettles.

CHEMICAL CONTROL

Chemical control on the Igepon T operation is relatively simple. During many years of processing experience, General Aniline has accumulated rule-of-thumb knowledge which tells the operators whether the reaction is going properly. At some points analytical samples are taken merely as a precaution and only analyzed if trouble develops later in the operation.

The phosphorus trichloride used for the production of the oleic acid chloride is generally accepted on the manufacturers' shipping analysis. Only spot checks are made of this material at about 3-month intervals. Every shipment of oleic acid, however, is analyzed against the specification given in the preceding section.

A complete analysis is submitted by the intermediates depart-

TABLE II. SERVICE REQUIREMENTS

(Per batch)

Process	Electric Power, Kw-Hr.	Steam, Lb.	Water ^a , Cu. Ft.
Oleic acid chloride	50	6000	150
Igepon T gel	330	9000	1200
Igepon T powder	1250	27000	800
Mixing ^b	130

^a Includes both process and cooling water.^b When ground and perfumed for direct consumption. Also sometimes used to blend two or more batches to give uniform product.

ment with each delivery of *N*-methyltaurine. Only the *N*-methyltaurine content figure of this analysis is checked by the Igepon operating section. From this figure the weight of the initial *N*-methyltaurine charge to the kettle is calculated. Samples for this check are taken both from the tank wagon and from the storage tanks. As an added precaution another sample is taken from the reaction kettle after the *N*-methyltaurine has been introduced and diluted with water. This sample is only analyzed if trouble develops later in the process.

The acid chloride charged to the reaction kettle is analyzed for oleic acid chloride, phosphorus trichloride, and free fatty acid.

After the condensation is complete the batch is checked for pH and residual *N*-methyltaurine. The pH is checked by a standard calomel-cell pH meter and is then adjusted as explained in the operating procedure.

After the pH has been adjusted it is checked again, and the final shipping sample is sent to the laboratory. This final sample is examined for clarity, viscosity, and alkalinity. A 10% water solution of this sample must be perfectly clear and must have a pH between 7.2 and 7.5 at this point.

The Igepon T powder undergoes an almost identical analysis routine. If its content of oleoylmethyltaurine falls outside of the permissible limits it is blended into subsequent batches at the ribbon blender.

UTILITIES

Since the Linden Works is a highly diversified operation involving a multitude of small capacity process installations, it is most economic to provide centralized utility installations to service all the individual plant areas.

Steam is produced in a central power plant and made available throughout the plant at both 90 and 450 pounds per square inch gage pressure. In the Igepon process steam is used only for process heating (Table II). Since the temperatures required are all reasonably low, only the low pressure steam is required for this operation.

All pumps and other auxiliary machinery are electrically driven. The motors run on 220-volt current supplied by a central steam-driven generator; 110-volt current is available in the operating buildings, but it is used for lighting only.

Compressed air is supplied by central compressors located in the power house. Separate lines carry 45- and 110-pound-per-square inch air throughout the plant. Since the Igepon operation requires air only for forcing liquids from one vessel to another, the 45-pound air is sufficient. This pressure produces a lift of about 100 feet for the liquids handled and even over considerable distances is adequate for the requirements of the process. In other parts of the plant the 110-pound air is used primarily for air-driven machinery and tools.

The air used for transferring phosphorus trichloride is passed through a dryer and filter to prevent hydrolysis and contamination. The purifying unit consists of a liquid trap, a steel chamber 12 inches in diameter and 6 feet long filled with quicklime to dry the stream, and a similar tank 4 feet long containing a cloth bag filter to remove any particles of lime or other solids that might be carried over into the phosphorus trichloride tanks.



Polyethylene-Lined Lever-pak Drums Are Being Tested to Replace Wooden Barrels for Shipping Igepon T Gel

The spray dryer has its own compressor which provides 90-pound-per-square inch air for atomization. This compressor was installed before the distribution lines from the central air supply were extended into the Igepon process building. Since the dryer is designed to use 90-pound air the independent compressor has been kept in service.

An unusual combination of circumstances operating at the Linden Works make the water supply situation there almost unique. The plant site is a low point of land extending out into Arthur Kill, a brackish arm of the sea, characteristic of the topography of the northern New Jersey coast. The water in this inlet analyzes from 7000 to 19,000 p.p.m. of chloride and from 14,000 to 20,000 p.p.m. of total dissolved solids. It has an average specific gravity of 1.015 as compared to 1.025 for sea water. A typical analysis might run:

	P.P.M.
Chloride	15,000
Magnesium	637
Calcium	254
Sulfate	1,253
Alkalinity (as CaCO ₃)	85

This brackish water, about one third as salty as sea water, is used for most cooling purposes in the Linden Works. The original decision to use salt water for cooling purposes was influenced by several factors in addition to its easy availability. The land point on which the works stand is occupied only by the chemical plants that grew out of the Grasselli Chemical Company. Fresh water for these plants is furnished by the municipality of Elizabeth, N. J. A single 14-inch line reaches out from the town of Linden to supply these works. This arrangement makes the

TABLE III. REPRESENTATIVE TYPES OF IGEPON T CURRENTLY MANUFACTURED

Product Name (General Dye-stuff Corp.)	Product Name (General Aniline & Film Corp.)	Raw Materials		% Active	Descriptive Data
		Fatty Acid	Taurine		
Igepon TN Gel	Antaron L-113	Oleic	N-methyl	13.5	Gel: pH 5% soln., 7-7.5
Cyclopon GA Ex	Antaron L-217	80 Palmitic 20 Oleic	N-methyl	13.5	Dense powder, cut with sodium sulfate
Igepon T Gel	Antaron L-114	Oleic	N-methyl	15.75	Gel: pH 5% soln., 7-7.5
Igepon T Gel Clear		Oleic	N-methyl	15.75	Clear gel: pH 5% soln., 8
Igepon TP Gel	Antaron L-110	Oleic	N-methyl	15.75	Soft gel: pH 5% soln., 6.6-6.8
Cyclopon A Ex	Antaron L-215	80 Palmitic 20 Oleic	N-methyl	15.75	Dense powder, cut with sodium sulfate
Igepon TC		Coconut	N-methyl	22	Paste slurry
Igepon TL Clear	Formula AG	Oleic	N-methyl	25	Clear liquid
Igepon NF ^a	Antaron L-520	Palmitic	N-cyclohexyl	28	Paste, nonfoaming
Igepon T Slurry	Antaron L-121	Oleic	N-methyl	28	Cloudy liquid
Igepon T Paste	Antaron L-130	Oleic	N-methyl	31.5	Paste
Igepon T Powder	Antaron L-135	Oleic	N-methyl	31.5	Fluffy powder, cut with sodium chloride
Cyclopon A Ex	Antaron L-245	80 Palmitic 20 Oleic	N-methyl	48	Dense powder, cut with sodium sulfate
Igepon LM Conc.	Antaron L-455	Lauric	N-methyl	60	Dense powder
Cyclopon A Powder High Conc.	Antaron L-265	80 Palmitic 20 Oleic	N-methyl	65	Dense powder
Igepon TFS Conc.	Antaron L-177	Oleic	N-methyl	72.5	Dense coarse powder

^a Patent pending.

fresh water expensive and General Aniline officials believe that it would be impossible to obtain any appreciable amount of additional fresh water from the water district at any price because of inadequate supply.

The cooling salt water intakes are located 24 feet below mean water. Temperatures at this depth are consistently low which improves the cooling efficiency of the water and eliminates the introduction of marine algae into the cooling systems. On only one occasion has the plant been troubled with marine growth inside cooling equipment. This occurred during a period of extreme turbulence at the intakes caused by nearby dredging operations.

The salt water intakes are protected by 16-inch-mesh rotary screens which are kept clean by water sprays. Other screens located in the various processing areas of the plant provide additional protection against the introduction of solid matter into the process equipment. An average of 5000 gallons per minute is taken through the intakes. However, during the summer this volume may rise to as much as 9000 gallons.

The chemical composition of this cooling water is such that its corrosivity has not proved as great a problem as its tendency to form a heavy adherent scale. To allow for this scale formation all cooling equipment in the plant has been intentionally over-designed. Performance data give an index of the decrease in heat exchange efficiency in such equipment as scale accumulates. When performance characteristics drop to predetermined empirical levels the coils or jackets are taken out of service and cleaned. Generally such cleaning is required only every 1.5 or 2 years. However, the cleaning must be done by mechanical means since the type of scale formed cannot be dissolved by ordinary acid or alkali cleaning techniques.

The use of once-through salt water instead of recirculated cooling water has another advantage for the Linden operations. Many of the waste effluents from dye and intermediates syntheses at the plant would normally present a serious waste disposal problem. However, under the present arrangement all liquids, process effluents, or cooling water are collected in a common sewer and returned to the kill. The large volume of used cooling water introduced into this sewer so dilutes the combined effluent that it is not necessary to treat the waste liquor before it is discharged.

MATERIALS OF CONSTRUCTION

The corrosion problem is not critical in the operations described, but some special materials must be used. Carbon steel is suitable for most vessels. However, those which must contain phosphorus trichloride or oleic acid chloride are homogeneously lead-lined. This type lining is applied by tinning the entire inner surface of the steel vessel and then soldering the lead

lining plates to the whole steel surface. This technique eliminates the problem of buckling and blistering. It also means that in the event of failure of the lining only the steel directly behind the gap in the lining is attacked. In the so-called "loose-lining" technique in which the lead sheets are tacked to the shell only along the seams, a failure at any one point usually means that the corrosive contents of the vessel will shortly enter the entire space between the lining and the vessel wall. Actually, the spray dryer feed tank at Linden is lined in this fashion, but only moderate temperatures are encountered in this tank and the agitation is never violent.

The lead linings in the Igepon process equipment last 7 to 9 years before they must be replaced.

The newest of the two Igepon reaction kettles is made of stainless steel. This kettle has proved satisfactory, and any future kettles installed for this step will be this type. However, the older kettle, lined with common glazed floor tile has given fairly good service, although as in all brick-lined kettles, the mortar is the weak point from a corrosion point of view. This brick lining requires pointing about every 2 years. All equipment which comes in contact with finished liquid Igepon is made of stainless steel, since the detergent will exchange cations with ordinary steel to form the iron salt which has an undesirable dark color.

Submerged steam lines in the brick-lined kettle are stainless steel; in the spray dryer feed tank these are lead. The other kettles are equipped with external jackets. Agitators are either lead-covered, stainless steel, or in the case of the old spray dryer feed tank, wooden.

Neither stainless steel nor lead will stand up in the duct which carries the moist exhaust from the spray dryer. Nickel is currently used for this service although tests indicate that a high nickel alloy (2E, 3E) would serve as well. The spray dryer itself is made of plain carbon steel.

Tanks which must withstand static pressure such as those employing air pressure transfer are entered and inspected, and subjected to hydraulic testing every 2 years. Unpressurized steel tanks which store corrosive liquids are on a similar inspection schedule. Storage tanks in noncorrosive service are inspected every 5 years. Kettles are also inspected at 5-year intervals. Jacketed kettles are lifted out of their jackets, and the surfaces are cleaned and inspected for pits. Pits usually occur in the welded seams. If the welds are badly pitted below the surface of the adjacent plates the bead is chipped off and the seam re-welded.

Pumps. Since most of the materials involved in the Igepon process are transferred through the plant by air pressure, pumps present only a limited corrosion problem. Where pumps are used they are of motor-driven centrifugal type. Where pure oleic

acid must be pumped, a high alloy steel (5E) pump is used. All other pumps are of carbon steel.

Valves and Pipe. Stainless steel valves are used on all lines which transfer finished liquid Igepon T. In the past other flows have been controlled by lead-lined plug valves. However, as these valves are retired from service they are being replaced with high chrome alloy gate valves (5E). Pipe lines which carry liquid Igepon T also are of stainless steel. Those which transfer oleic acid chloride are lead-lined and steam-traced. The steam tracing is only used in the winter when the acid chloride has a tendency to thicken and move sluggishly.

NEW PLANT

Construction is just beginning on a new plant to replace some of the facilities described in this article. Additions are being made to an existing new building which will ultimately house the manufacture of Igepon T gel, an Igepon T liquid which has just recently been submitted to the market, and a slurry form which is now in the process of market introduction. The processes employed in the new installation will be identical to that now in use. The two reaction kettles and all piping and equipment which will handle the finished Igepon will be made of stainless steel.

The new facilities will accommodate only the final step of the Igepon production. *N*-methyltaurine will continue to be made by the intermediates department of the company and the oleic acid chloride will be produced in the equipment now used for that purpose.

IGEPO T PRODUCTS

Igepon T finds its greatest use today in the textile field where it was first introduced. The approximately 65% of sales that go into this industry find their way into almost every phase of textile wet processing. The list of uses include scouring, wetting out, degumming, kier boiling, dye leveling, dye pasting, chlorine and peroxide bleaching, fulling, lime soap dispersing, and finishing. Agriculture, paper, leather, and metal cleaning consume most of the remaining 35% of sales. Small amounts of Igepon T go into household products, including dentifrices, shampoos, cosmetics, and pharmaceutical preparations. It is also used in the scouring of feathers, in electrolytic plating baths, in the washing of automobiles, airplanes, railroad coaches and locomotives, rugs, floors, buildings, and for cleaning streets and roads, and in the dairy, food, and fur industries.

Shortly after General Aniline began production of Igepon T it was discovered that the product could be produced in gel form. The optimum surfactant concentration for gelling was near one half that of the standard paste or powder so that when this product was ultimately marketed its strength was standardized at 15.75% oleoylmethyltaurine for the sake of uniformity and ease in accounting practice. The second year the gel was on the market its sales exceeded those of the paste form and it has continued to supplant that product until paste sales are now almost negligible.

In 1942 Igepon TFS was introduced largely in response to a request by the Navy for a powder of high active concentration for use aboard ship and for shipment to advance bases. The product developed to meet this demand contained 72.5% active ingredient. In the last 2 years of World War II the Navy shifted over to the standard powder. However, by that time the TFS had begun to find a civilian market and was retained in the line of Igepon products.

General Aniline has developed two new forms of Igepon T which are now ready for the market. One is a clear liquid suitable for incorporation into consumer products. It looks much like a conventional liquid soap and is available with 15 and 25% active ingredients.

The newest of the products is called a "slurry" although it more nearly resembles an opaque heavy liquid. This material



Phosphorus Trichloride Is Stored Outside the Processing Building as a Safety Precaution

contains 28% active ingredient and is essentially the product as it comes from the condensation kettles; it contains no added chemicals. The material is intended primarily for formulators who will process it further by adding it to other ingredients or drying it to a powder. It can be shipped in tank cars and is the least expensive of the various Igepons.

As of last spring General Aniline made the primary reactant of Igepon T, *N*-methyltaurine, available to the general public. This compound has never before been commercially available in this country. Since the basic patent on Igepon is about to expire, other organizations may undertake the manufacture of Igepon-type products. In this event General Aniline can supply the manufacturers with *N*-methyltaurine and other taurine derivatives. There is, of course, one restriction. The would-be manufacturer must use a new name for his surfactant. The name Igepon is registered by the General Dyestuff Corporation, an independent organization selling General Aniline's dyes and surfactants. Not even the General Aniline company itself may use the name when it makes a sale through its own sales department. The product then becomes Antaron, a trademark of General Aniline's Antara division (Table III). Thus Antaron L-114 is Igepon T gel, Antaron L-130 is Igepon T paste, Antaron L-135 is Igepon T powder, and Antaron L-177 is Igepon TFS High Conc.

The Igepon T series using oleic acid and *N*-methyltaurine as starting materials must not be confused with the Igepon A series which is made from oleic acid and hydroxyethanesulfonic acid. The Cyclopon A series of products are Igepon T types made from palmitic acid and *N*-methyltaurine. Igepon NF is also a taurine-

TABLE IV. INVERSE WETTING STRENGTH OF TAURINE-TYPE IGEPON IN DISTILLED WATER

(Draves wetting tests: 25-second sinking time at 25° C.; 3.0-gram hook)

Igepon	Active Material Req'd., Grams/Liter
Sodium <i>N</i> -2-ethylhexanoyl- <i>N</i> - <i>n</i> -butyl taurate	>7.50
Sodium <i>N</i> -octanoyl- <i>N</i> - <i>n</i> -butyl taurate	>5.00
Sodium <i>N</i> -2-ethylhexanoyl- <i>N</i> -cyclohexyl taurate	10.00
Sodium <i>N</i> -heptanoyl- <i>N</i> - <i>n</i> -octyl taurate	0.49
Sodium <i>N</i> -octanoyl- <i>N</i> - <i>n</i> -octyl taurate ^a	0.29
Sodium <i>N</i> -2-ethylhexanoyl- <i>N</i> - <i>n</i> -octyl taurate ^a	0.61
Sodium <i>N</i> -decanoyl- <i>N</i> -cyclohexyl taurate ^a	0.84
Sodium <i>N</i> -decanoyl- <i>N</i> - <i>n</i> -heptyl taurate ^a	0.19
Sodium <i>N</i> -decanoyl- <i>N</i> -2-ethylhexyl taurate ^a	0.16
Sodium <i>N</i> -decanoyl- <i>N</i> - <i>n</i> -octyl taurate ^a	0.21
Sodium <i>N</i> -(9-undecenoyl)- <i>N</i> -methyl taurate	6.75
Sodium <i>N</i> -(9-undecenoyl)- <i>N</i> - <i>n</i> -octyl taurate ^a	0.30
Sodium <i>N</i> -dodecanoyl- <i>N</i> -methyl taurate	9.50
Sodium <i>N</i> -dodecanoyl- <i>N</i> -ethyl taurate	2.50
Sodium <i>N</i> -dodecanoyl- <i>N</i> -isopropyl taurate	0.62
Sodium <i>N</i> -dodecanoyl- <i>N</i> - <i>n</i> -propyl taurate	0.50
Sodium <i>N</i> -dodecanoyl- <i>N</i> -isobutyl taurate	0.41
Sodium <i>N</i> -dodecanoyl- <i>N</i> - <i>n</i> -butyl taurate	0.38
Sodium <i>N</i> -dodecanoyl- <i>N</i> -(mixed) amyl taurate ^a	0.21
Sodium <i>N</i> -dodecanoyl- <i>N</i> -hexyl taurate ^a	0.18
Sodium <i>N</i> -dodecanoyl- <i>N</i> -cyclohexyl taurate ^a	0.26
Sodium <i>N</i> -dodecanoyl- <i>N</i> - <i>n</i> -heptyl taurate ^a	0.33
Sodium <i>N</i> -dodecanoyl- <i>N</i> -2-ethylhexyl taurate	0.28
Sodium <i>N</i> -dodecanoyl- <i>N</i> - <i>n</i> -octyl taurate	0.46
Sodium <i>N</i> -tetradecanoyl- <i>N</i> - <i>n</i> -butyl taurate	<1.00
Sodium <i>N</i> -tetradecanoyl- <i>N</i> -(mixed) amyl taurate ^a	0.25
Sodium <i>N</i> -tetradecanoyl- <i>N</i> -cyclohexyl taurate	0.55
Sodium <i>N</i> -tetradecanoyl- <i>N</i> -hexyl taurate	0.30
Sodium <i>N</i> -hexadecanoyl- <i>N</i> -methyl taurate	1.45
Sodium <i>N</i> -hexadecanoyl- <i>N</i> - <i>n</i> -butyl taurate	1.45
Sodium <i>N</i> -hexadecanoyl- <i>N</i> -(mixed) amyl taurate	0.75
Sodium <i>N</i> -hexadecanoyl- <i>N</i> -cyclohexyl taurate ^a	1.43
Sodium <i>N</i> -(9-octadecenoyl)- <i>N</i> -methyl taurate	1.50
Sodium <i>N</i> -(9-octadecenoyl)- <i>N</i> -ethyl taurate	0.91
Sodium <i>N</i> -(9-octadecenoyl)- <i>N</i> -(mixed) amyl taurate	2.25
Sodium <i>N</i> -(9-octadecenoyl)- <i>N</i> -cyclohexyl taurate	4.00

^a Patent pending.

derived compound prepared from palmitic acid and *N*-cyclohexyltaurine. Similarly, Igepon LM is made from lauric acid and *N*-methyltaurine.

THE FUTURE OF IGEPONS

The past 20 years represent only the introductory stage in a development of surface-active products and their uses. The increased amount of research in both synthesis and application currently sponsored by large chemical manufacturers and the petroleum and soap companies assure the continuing development of both new products and new uses. It cannot be predicted with certainty which one of these two lines of research will have the greatest effect on the future growth of sales. These two efforts combined are pushing the sales saturation point far ahead and can be expected to continue this trend for many years to come.

The future for Igepon T, its analogs and homologs, is bright. The economic existence of this type surfactant is assured by the fact that the biggest weight in its molecule is a fatty acid. The principal fatty acid used is oleic acid which is found abundantly in vegetable and animal fats. As synthetic detergents derived from nonfatty sources encroach on the soap market, the fats and particularly tallow from which oleic acid is largely derived will tend to become more and more a surplus product. Igepon, a fat-derived surfactant, should benefit economically by this development.

Another advantage enjoyed by the taurine type Igepon (*N*-acyl-*N*-alkyl taurates) is the fact that the Igepon T gel, largest seller in the group today, is not the best wetter in the series, nor is it the best emulsifier or dispersant. It is not the best foamer, the best textile-softening agent, or lime-soap dispersant, nor is it the most soluble member of the group. It has a good high average on all counts which led its German inventors and American developers to call it the "universal soap." However, surface-active agents today are being developed to accentuate maximum efficiency in one direction. Thus wetting may be increased at the sacrifice of other properties if wetting is what is desired. Perhaps no foam or low solubility is desired. As explained, the

taurine-type Igepon (Table IV) can be modified to well over 1000 varieties. Any one of the various detergent properties may be obtained to a high degree by making changes in the structure of the Igepon molecule. Consequently, it is predicted that the Igepon-type surfactants will have an important future in the development of special purpose products where price is not the primary consideration.

Future sales will depend not only on development of new specialty surfactants but on development of new large scale uses. Two of these have already made a start: the admixture of surfactants to soap to produce new and better household cleaners and the use of surfactants to improve the operation level of industrial chemical processes.

Chemical industries have a big surprise in store when they begin to use the tool kit of surface-active agents. Manufacturers will learn that the surfactants in chemical processes may be as important as catalysts. A surfactant may increase the yield of a chemical product or purify it, or do both. It can condition a raw material for reaction, increase speed of filtration for some chemicals, and induce faster crystallization in others. The General Aniline & Film Corporation believes that there will be much development in this direction and has undertaken to train personnel in the use of surfactants in chemical processes.

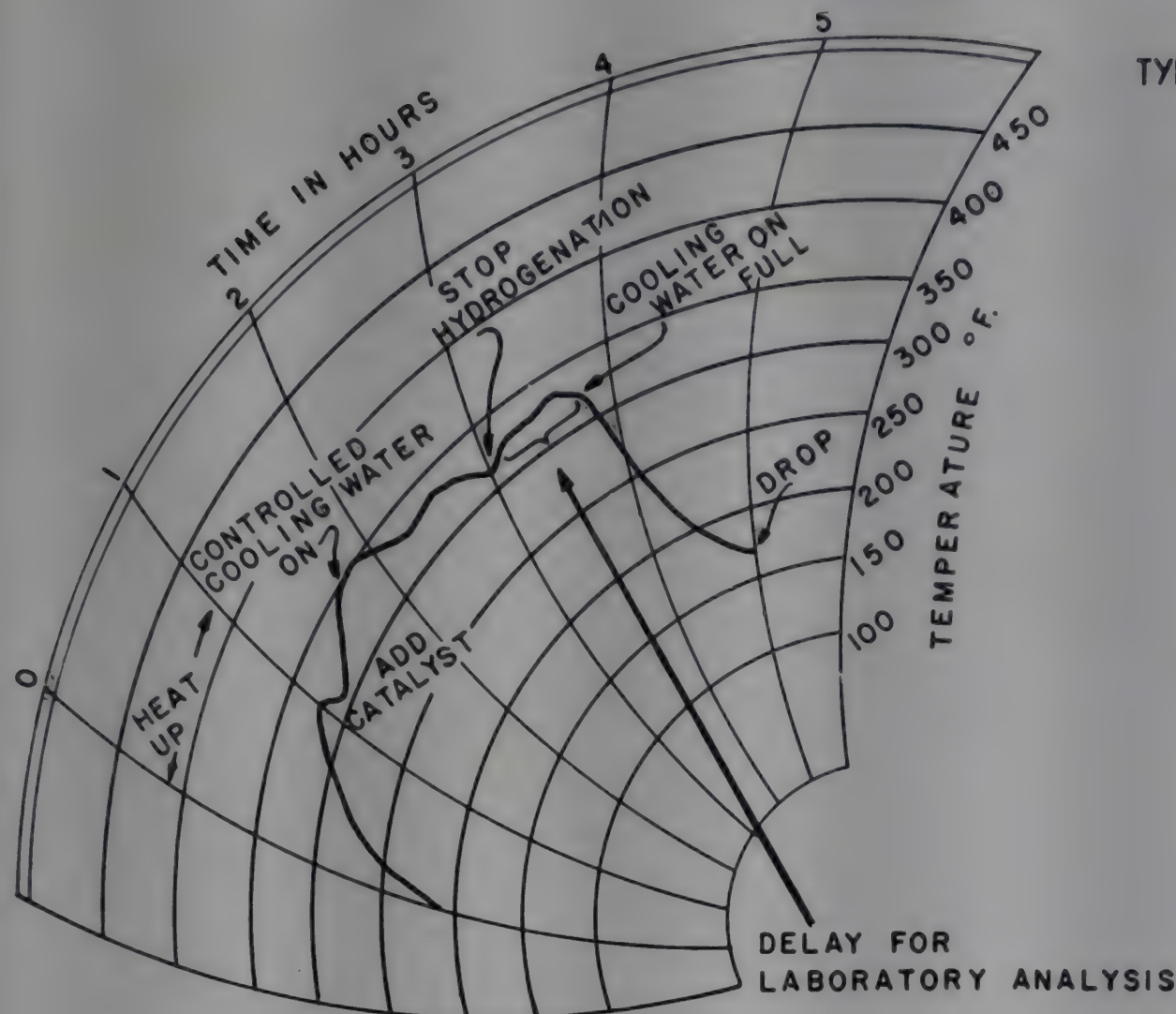
Soap in its battle with synthetic detergents may find that it has its back to the wall. It is fighting a mighty battle on the sheer strength of its foaming and cleaning power and low price. But it has few, almost no analogs and homologs to call on, whereas the synthetic detergents have hundreds of patents with millions of newer products awaiting development. Soap, however, has one way out and that is, to mix itself with one of these synthetic detergents. Detergents were made and investigated for their value per se, but today research is endeavoring to find suitable and compatible companions for soap. This development may prove a life-saver for soap. It may also provide a major market for Igepon-type surfactants which in general can be incorporated into soap-containing products.

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EDIBLE OILS

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THE production of edible vegetable oil products in this country is big business. Combined output of these for 1949 amounted to approximately 3.5 billion pounds, about 20 pounds per capita and almost 30% of the country's entire production of all fats and oils. This represents an increase in consumption of more than 100% in the last generation.

There are two classes of edible oils and fats, liquid oils and plastic fats; the plastic fat group is used to the largest extent in the western hemisphere, largely because of the meat-eating proclivities of the peoples and the availability of fats from the animals eaten. Vegetable shortening, which has all the physical characteristics of a plastic fat, is strictly an American invention; it is a child of cotton farming that has grown out of the need for new products from cottonseed oil.

Up to a few years ago cottonseed oil was the preponderant oil as far as usage was concerned. This was largely a question of availability, but large scale crushing of soybeans has changed the picture. In 1948, 707,000,000 pounds of soybean oil were used for shortening manufacture, as compared with 325,000,000 pounds of cottonseed oil (26). In margarine, the other plastic fat consumed in largest quantity, soybean oil is also giving cottonseed oil a race. In 1946 the ratio was 223,000,000 to 201,000,000 pounds of cottonseed to soybean oil, respectively (25), but cottonseed has again climbed until the ratio is now about 2 to 1. Salad and cooking oils may be made from cottonseed and soybean oil, and cooking oil from peanut oil. Weber and Alsberg (28) cover the historical background of the American shortening industry very thoroughly; Snodgrass (23) does the same for margarine and Bailey (2) for refining problems. The intention of this article is not to give an account of this industrial development but to cover the operations of a modern processing plant.

The modern plant for processing edible vegetable oils into food products is indeed a complex one, principally owing to three factors: The first is the variety of starting raw materials, which may be cottonseed oil, soybean oil, peanut oil, or any combination of these three. Secondly, whatever the oil, it must be subjected, as a raw material, to a number of treatments before it can either be considered as a finished product or can be made into a finished product. Finally, any one of a variety of products may be made from each type of oil after it has been treated. Figure 1 is an integrated diagram of the processing steps and those involved in the manufacture of finished food products.

SHERMAN, TEX., PLANT OF MRS. TUCKER'S FOODS

The plant of Mrs. Tucker's Foods at Sherman, Tex., is considered an excellent example of a modern vegetable oil processing plant. Since its organization 36 years ago as the Interstate Cotton Oil Refining Company, it has kept well abreast of the latest developments in the oil processing field and has pioneered in some lines. Production of cooking oil, manufactured by the old batch "kettle" method, began on October 16, 1913, with a capacity of 1 tank car of oil per day. In 1934 the company installed one of the first centrifugal refining units used in the South by the vegetable oil industry. (Cudahy Packing Company put the first into operation in 1933 at Memphis, Tenn.; Mrs. Tucker's started installation in 1933 and began operation the following year.) Shortly after that the first units of a hydrogen gas plant and a hardening plant were completed. Up to that time requirements of hydrogenated oils for standard shortenings had been purchased from other manufacturers.

In 1947 the company changed its name to Mrs. Tucker's

Foods, Incorporated, to conform to the brand name of its major products. A continuous vacuum deodorization system was added to the old batch operation, and in 1949 a complete new unit, housing a continuous soda ash refining system and the continuous vacuum bleaching system, developed by plant engineers over the previous 8-year period, was put into operation.

REFINING

The vegetable oils and fats are composed largely of glycerides of the saturated and unsaturated fatty acids (notably oleic and linoleic) with some free fatty acids and materials causing odor and color. The free fatty acids are usually produced in the seeds themselves by enzymatic hydrolysis before extraction of the oil but, infrequently, develop during the extraction process. Whatever their origin, the purpose of the refining step is to remove them and also whatever undesirable coloring there may be.

There have been many individual techniques used in vegetable oil refining, but other than the use of some high vacuum distillation units in Europe (14) (operation of which is similar to American techniques used in the deodorization step), they have all consisted fundamentally of saponification of the free fatty acids and removal of the gums, followed by separation of the soap stock or foots. The European distillation units are small in size, produce a relatively dark-colored oil, and are not suitable for use with soybean, cottonseed, and other vegetable oils which contain phosphatides.

Alkali refining was a batch process for a long time and for many years the industry depended entirely on caustic soda as the alkaline medium. In the last 15 years, however, the Clayton processes (10) have been placed in efficient practice by most of the refiners in this country. The basic process makes use of centrifuging instead of kettles for separating the soap stock from the oil. As Goss (13) points out, the centrifugal separation method, which contributes to a higher yield of neutral oil, represents a great advance over the older kettle processes. A later modification (11) in the Clayton processes involves the substitution of soda ash for caustic soda during the greater portion of the refining. The main advantage claimed for this modification is the reduction of refining losses. Caustic soda reacts with some of the neutral oil as well as the free fatty acids, resulting in a loss of good oil with the foots. The use of soda ash largely eliminates this disadvantage. In general, it appears that a refining loss reduction of approximately 20% is made in going from the batch method to the continuous, and a further reduction of 15% is made by substitution of soda ash refining for the straight caustic process. Tyler (24) gives some industrial data in this regard. Mrs. Tucker's Foods has housed the new equipment utilizing the Clayton process (Figure 3), designed and installed as a complete unit (1A), in a new building of greater than 25,000 square feet in area.

RAW MATERIALS

Soda ash is received in bags, dissolved in water in a 4000-gallon, air-agitated tank to a 20° Bé. solution, and stored in a second 4000-gallon supply tank, also air-agitated. Caustic soda is received as 72° Bé., and sufficient water is added during the unloading to give the lowest freezing point consistent with easy pumping. It is then diluted with water as needed to a 20° Bé. solution and is stored in an air-agitated 2000-gallon supply tank.

Crude cottonseed or soybean oil (Mrs. Tucker's seldom processes peanut oil) is pumped from agitated storage tanks (capacity 7,000,000 pounds) to two 140,000-pound crude oil supply tanks equipped with motor-driven agitators and steam coils and mounted on scales. Refining losses are determined entirely by weighing the crude oil going into the process and the refined oil recovered. The oil is first pumped through a strainer (3A) to an indicating flowmeter and thence through the tube side

of a one-pass economizer and the shell side of a steam heat exchanger.

Because the refining process is a continuous one, continuous and accurately metered flow of raw materials into the neutralizers or saponifiers and later operations is essential. To accomplish this the raw materials are all fed through a metering device consisting of four piston-type pumps. The length of stroke on the pump carrying the crude oil is kept constant.

Two pumps deliver soda ash, one to the neutralizers and one to the rehydration mixer, and a third delivers caustic soda to the re-refine mixer. These three pumps are set to deliver a fixed proportion by volume of soda ash and caustic soda in relation to the amount of crude oil, and the total quantity of raw materials delivered at different points in the refining process may then be varied by adjusting the flow through the metering device as a unit, with the desired proportions of raw materials to each other maintained at all times.

SAPONIFICATION

Saponification may be a somewhat misleading term as applied to alkali refining, although it is quite generally used. Actually, removal of the gums in oils is probably just as important as removal of the free fatty acids, and it is only in those plants where the free fatty acid content of the crude oil is from 2.5 to 5% that saponification assumes the major role. As received by Mrs. Tucker's, crude soybean oil usually contains less than 1% free fatty acids and crude cottonseed oil about 1.25%. Therefore the plant is more concerned with gum removal.

Crude oil and soda ash (3% by weight of the oil) are delivered to the neutralizing mixers. These mixers are 63-gallon mild steel tanks, 12 inches inside diameter and 6 feet high; agitation is by paddle-type stirrers revolving between fixed blades. Heat is

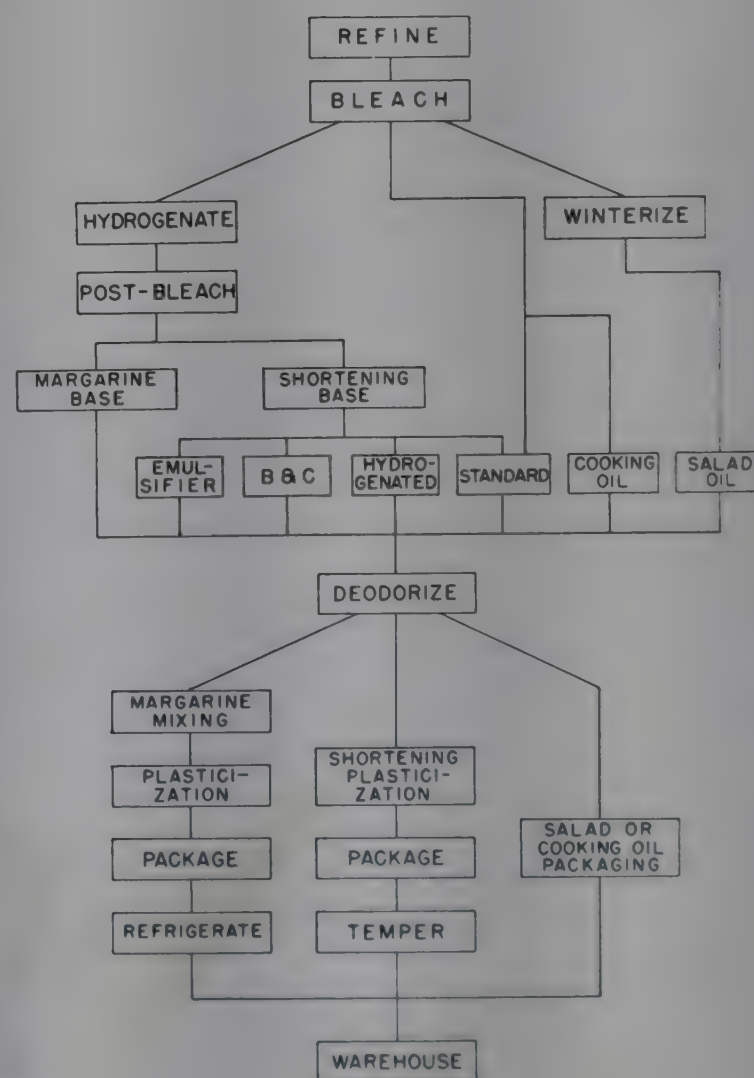


Figure 1. Flow Sheet of Processing and Packaging Steps

furnished by steam jackets, 150 pounds per square inch pressure. Other mixers used at various succeeding points in the alkali refining are similar in construction and differ only in provisions for heating. The neutralized oil and soap stock then pass into a series of concentric-tube heat exchangers, and thence at 210° F. into a dehydrator, which is heated by steam coils and is under a vacuum of about 29 inches of mercury. The condensate is discarded and the dehydrated oil is pumped at 160° F. to the steam-jacketed rehydration mixers. Screw-type pumps (1A) are used rather than centrifugal, because these operate more satisfactorily with a vacuum on the suction side. The dehydration-rehydration treatment is carried out to condition the soap stock for most efficient separation. Rehydration is accomplished by continuously adding 5 to 7% by weight of 20° Bé. soda ash from the feed metering pump to the oil, as it goes to the rehydration mixers.

After rehydration the oil is fed to the primary soap stock separators (1A). These separators and the neutralizers are shown in Figure 2. Soda ash solution (12° Bé.) is fed from a 1000-gallon tank to prime the centrifuges on initial start-up only, and is cut off after operating conditions have leveled off. This is in contrast to the procedure used in some plants where the soda ash flow to the centrifuges is maintained at all times. The crude soap stock drops down through spouts at the bottom of the centrifuges to a 12,900-pound tank from which it may be sold as such or further treated by acidulation or concentration. Mrs. Tucker's manufactured a brand of laundry soap until 1924, but since that time has sold the soap stock to other manufacturers. The oil layer, at 190° to 200° F., comes off the top and passes first through the shell side of the economizer, carrying the original crude oil on the tube side, and then through a water cooler where its temperature is reduced to 90° F. before it goes to the re-refiner. This cooling is a necessary prerequisite to the removal of final color.

Re-refining is necessary because the oil is still dark and would be difficult to bleach if it were not treated further, even though its free fatty acid content has been reduced to less than 0.05%. It is therefore given a caustic soda treatment similar to that practiced in conventional all-caustic refining, the principal difference being that the resins and other undesirable materials have already been removed. The caustic soda is introduced into the feed line to the re-refiner, so that it contacts the oil which is still cold. Heating to 160° to 170° F. is then accomplished in the re-refiner. Re-refining is not considered a major step in the process; it removes only a small amount of material from the standpoint of quantity but effects a significant color removal.

Heated oil from the caustic treatment is fed to another set of centrifuges, the re-refine or decolorizing separators. The gravity of the caustic soda in the oil is sufficiently high that centrifuging, as is, would result in a stratified mixture containing an oil phase, a soap phase, and a strong caustic phase, making separation difficult because of the wide difference in specific gravity of the phases. In order to overcome this difficulty the Clayton patents include a technique (11) developed by De Laval, involving the addition of water in varying amounts to the bottom of the centrifuge bowl. The added water rides up along the sides of the separator bowl (Figure 4) diluting the accumulation of strong caustic to a specific gravity equal to that of the soap phase. The soap phase then passes out of the bowl along with the dilute caustic, through the water phase outlet, and is discarded; the decolorized oil passes out of the oil phase discharge spout.

The oil layer, discharged at the top of the separators at 160° to 170° F., still has a soap content of 1000 to 2000 p.p.m. which must be removed. Hot water (16% of the oil feed) is added, the two are mixed thoroughly, and the mixture is heated to 190° F. in a concentric-tube heat exchanger. Final separation is carried out in another set of four centrifuges—the water-wash separators (1A). The soap-water phase from these last centrifuges contains about 2% soap and is discarded.

The oil layer from the water-wash separators still contains some moisture. Already at 190° F., it is flashed in a vacuum chamber (29 inches of mercury) to remove the water and is pumped through a water cooler, where it is cooled to about 150° F. It is then weighed in the refined oil scale tanks (two tanks, 140,000 pounds each) and pumped to storage. Approximately 20 minutes are consumed in the complete refining treatment. Approximately 0.4 pound of steam is required per pound of oil refined. Table I shows the analysis of a typical oil in the crude state and after refining. A typical refining loss for soybean oil is about 4.5% and for cottonseed oil, 6%. The actual poundage of waste material to account for this quantity is more than double the loss because of the sodium salts and added water. About 25% of the waste material is classified as total fatty acids, and only this amount may be considered to have any commercial value.

TABLE I. ANALYSIS OF TYPICAL OILS

Analysis	Cottonseed Oil		Soybean Oil	
	Crude	Refined	Crude	Refined
Free fatty acid, %	1.00	0.05	0.70	0.05
Color (Lovibond red)	..	6.2	..	8.5
Bleach color (Lovibond red)	..	2.0	..	2.7
Official refining loss, %	6.6	..	5.6	..

STRAIGHT CAUSTIC REFINING

The Sharples straight caustic refining system, which the soda ash process superseded at Mrs. Tucker's, is still available for service. This particular system consists of eight soap stock separators, six first water-wash separators, and five second water-wash separators. Centrifuges in this system have 4-inch diameter bowls compared to 16-inch bowls in the newer system. During periods when oil prices are low, the soda ash system has less economical advantage than it has when oil prices are high. In addition, soda ash soap stock must be further treated to be tenderable in accordance with minimum requirements for total fatty acids as required by present-day trading rules. This is not the case with straight caustic soap stock.

BLEACHING

For market acceptability, the refined oils must still be bleached. Mrs. Tucker's uses the conventional bleaching clays to adsorb the color pigments from the oil, but in contrast to batchwise kettle operation still practiced by many vegetable oil processors, plant engineers have developed a continuous bleaching technique, including vacuum treatment in the actual bleaching tower. This results in improved flavor and stability in the oil, removes more soap than does atmospheric bleaching, and does not allow as much increase in fatty acid content by hydrolysis.

The continuous bleaching method has recently been described in some detail in the literature (15). Briefly, it consists of pumping heated oil through opposed nozzles into a slurry tank and feeding bleaching clay into the nozzle streams to ensure thorough mixing. The mixture is sprayed into the upper half of a vacuum tower (28 to 29 inches of mercury vacuum). Here the gases dissolved in the oil and adsorbed on the clay are deaerated and some moisture is removed while oil temperatures are relatively low. The slurry is then heated to a higher temperature and sprayed into the bottom half of the tower, where bleaching takes place, and the bleached oil is recovered by filtering through closed aluminum plate-and-frame filters. Figure 5 shows the vacuum towers, one for cottonseed oil bleaching and one for soybean oil bleaching, with the filter presses in the foreground.

INTERMEDIATE OPERATIONS

All refined and bleached oil produced at the plant, whatever its intended end use, goes through the deodorization step. A

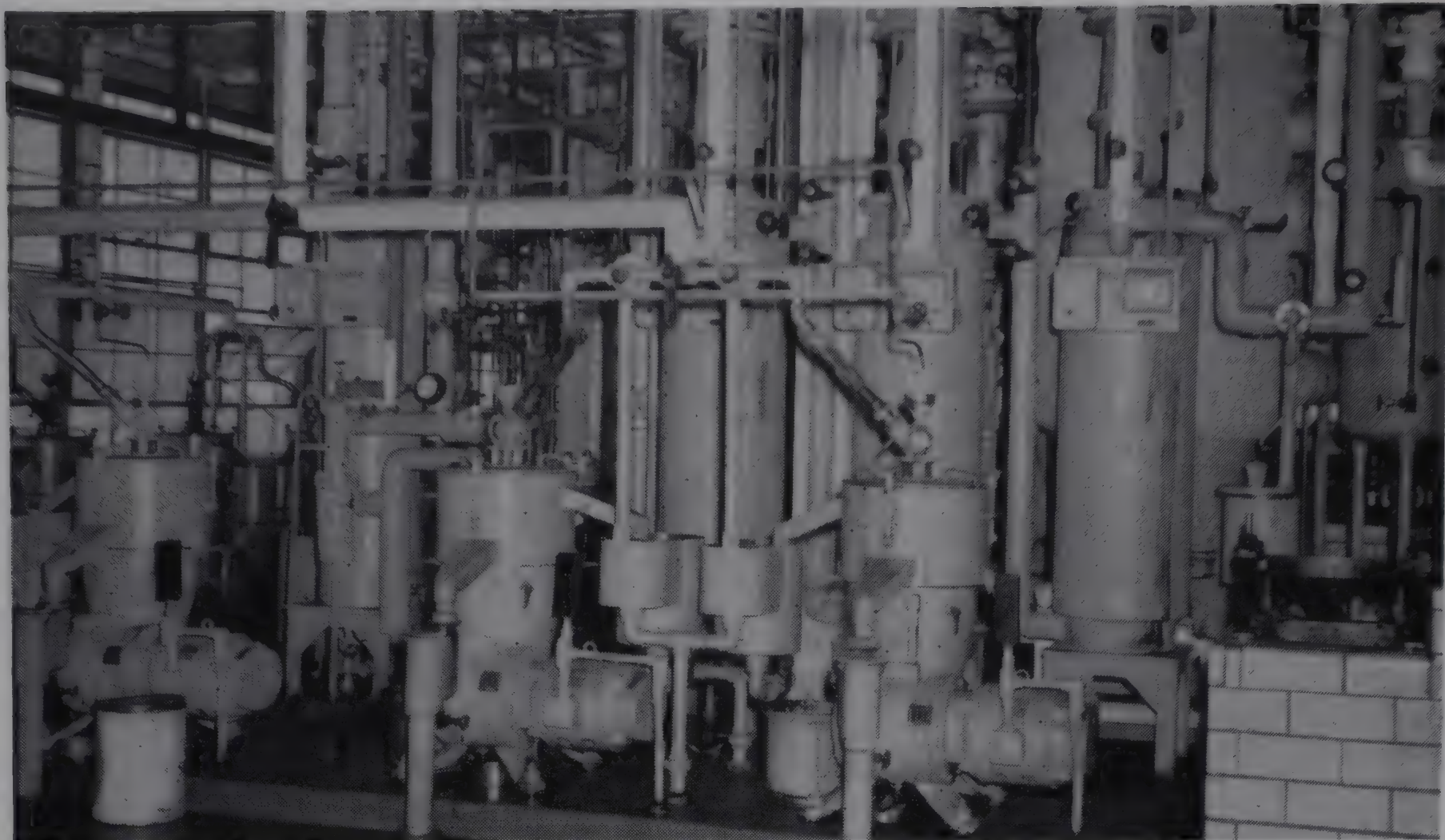


Figure 2. Neutralizers and Water-Wash Separators

large proportion of the oil, intended for margarine and shortening bases, is hydrogenated first. However, the portions intended for the following uses are not hydrogenated: (1) oil for mixing with hydrogenated oil to form standard shortening; (2) cooking oil; and (3) salad oil. Cooking oil is usually peanut oil or an unwinterized cottonseed oil, which congeals in the range 40° to 45° F., whereas salad oil, which has been given the special winterization treatment, remains substantially liquid in that temperature range and is thus able to give a mayonnaise emulsion stable at low temperatures.

For winterizing, the oil is pumped to narrow vertical rectangular steel tanks in a refrigerated room. The tanks are 2 × 8 × 33 feet, and hold 20,000 pounds each. Here the oil is chilled at 39° to 45° F. for 3 to 4 days. The natural hard constituents, or higher melting glycerides (15 to 25% of the oil), crystallize and are filtered out through plate-and-frame filters using cloth. The tanks are situated on the fourth floor and the filter presses on the first, with the result that a 15-pound-per-square-inch filter pressure can be obtained from the static head, eliminating the use of pumps which tear up the particles and slow down filtration rates. The material filtered off can be used in making stearin or standard shortening. The oil, evaluated by the A.O.C.S. winterization test (1), must remain clear for 5.5 hours when immersed in a sealed 4-ounce bottle in melting ice at 32° F. Most cottonseed oils, however, remain clear longer than that and up to 24 hours. After winterizing, the oil is then ready for deodorizing in the same manner as the hydrogenated oils.

HYDROGENATION

The vegetable oil industry was actually a stepchild of the meat packing industry until catalytic hydrogenation was introduced about 1910. The hydrogenation of fatty oils was the first catalytic hydrogenation process to be placed in operation, and it made vegetable oil processors independent. To produce fats of higher melting point and to reduce their tendency toward oxidation, it is customary to hydrogenate the oils partially and selectively to a degree dependent on the uses to which the hydrogenated product is to be put. Jamieson (16) defines selectivity

in this case as the reduction, to a considerable extent, of the more unsaturated acids, free or in ester form, before the less unsaturated acids begin to react. He says that in partial hydrogenation some stearic acid is formed along with considerable quantities of the so-called iso-oleic and oleic acids from the reduction of linoleic acid. Bailey (4) points out that hydrogenation should result principally in the reduction of linoleic to oleic acid, rather than oleic to stearic, and that the iso-oleic content should be minimized. Low temperatures favor the formation of stearic acid, but high temperatures favor formation of iso-oleic. The important thing is to reduce the linoleic acid content to a minimum without hardening the product above a desired melting point. This, in general, can be done by judicious use of catalyst and by varying the conditions of hydrogenation. Bailey, in a current article (6), discusses kinetics and theory of fatty oil hydrogenation.

Catalyst. The catalyst necessary for the hydrogenation reaction, which is conducted at somewhat elevated temperatures and under slight pressure, is a 25% nickel catalyst made by reducing nickel salts with hydrogen, in an oil solution with or without filter aid. It is purchased either in flaked form (6A), which is essentially the catalyst in a completely hydrogenated oil, or as a slurry in oil, or "frozen" into cakes (4A). Another important form of nickel catalyst, not used by Mrs. Tucker's, is known as Raney nickel (19). This is thought to consist of nickel hydride and is made by treating a nickel-aluminum alloy with caustic soda, thus dissolving out the aluminum as sodium aluminate.

It is important that the sulfides be removed from the gas being converted to hydrogen and that the concentration of carbon monoxide in the purified hydrogen be at a minimum, as only traces of these compounds will poison the nickel catalyst and reduce its usefulness. Wurster (30) states that carbon monoxide, under the influence of the catalyst, undergoes chemical reactions itself and thereby uses some of the catalyst in the reactions. He also states that the purity of the oil to be hydrogenated has a direct effect on catalyst consumption. Phosphatides in cottonseed oil and sulfur in soybean oil have a direct poisoning or an

CRUDE OIL REFINING

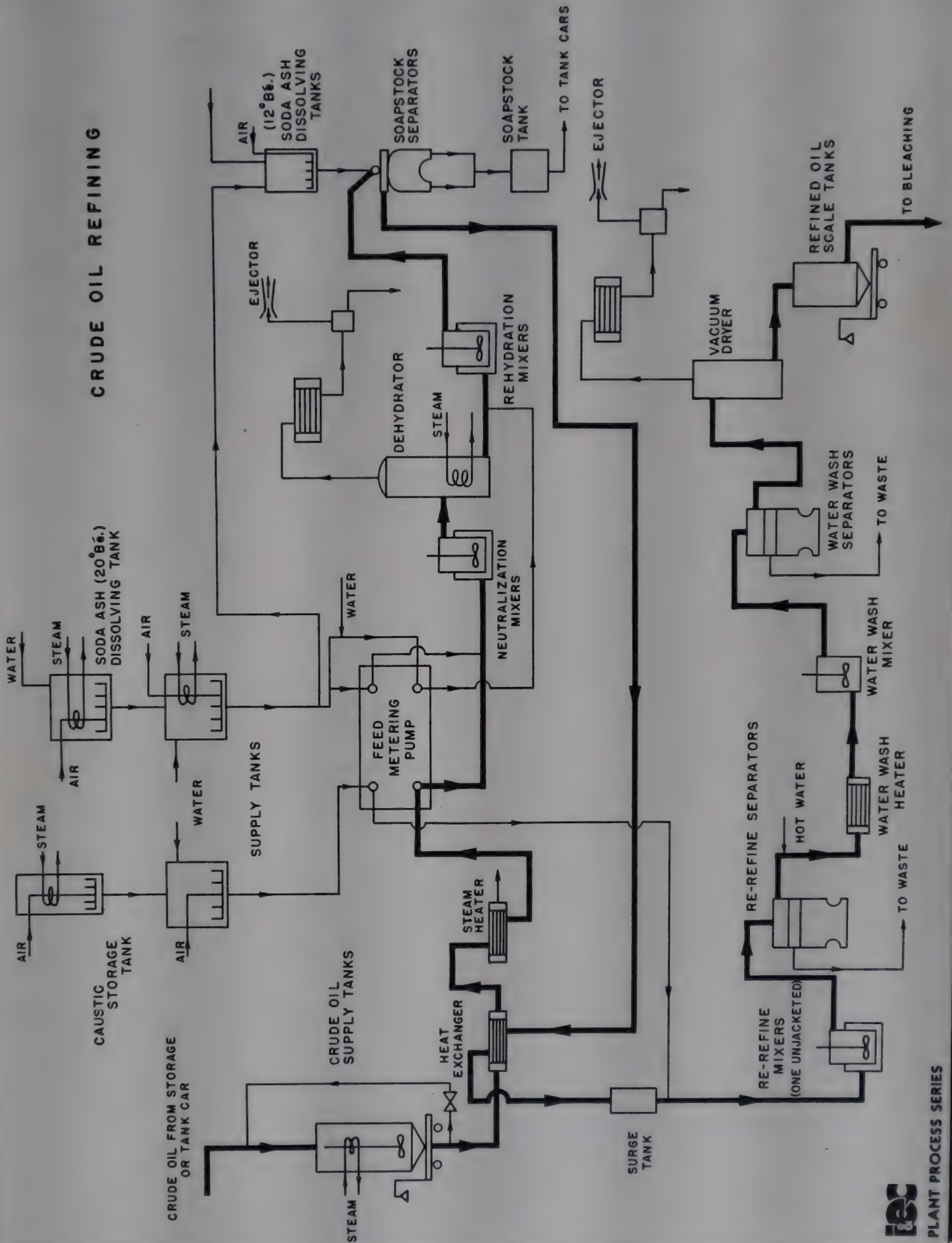


Figure 3. Flow Sheet of Refining Process at Sherman, Tex., Plant of Mrs. Tucker's Foods, Inc.

inhibiting effect on the catalyst. This fact is confirmed by the improvement noted since installation of the vacuum bleaching system which has resulted in reduction of these constituents. Another factor, which may have considerable future importance in regard to catalyst poisoning, is the use of solvent extraction processes involving trichloroethylene. A problem which has not yet been solved satisfactorily in these processes is the complete removal of solvent from the oil, and it has been the experience at Mrs. Tucker's that as little as 0.01% residual trichloroethylene in the oil will act as a catalyst poison.

Hydrogen Manufacture. In discussing the hydrogenation operation it is of considerable interest to give a full description of the source of hydrogen used. In Mrs. Tucker's plant, which has a hydrocarbon-steam reforming unit employing the most modern techniques, this is particularly so. Hydrogen may be manufactured by a number of methods, depending on the availability of raw materials and economic considerations. The most general methods are the electrolytic, steam-iron, water gas, and hydrocarbon-steam reforming processes. Electrolytic hydrogen is generally manufactured where low cost electricity is available, where both hydrogen and oxygen are desired, or where complete absence of carbon compounds is necessary. In the steam-iron process steam is passed over hot iron ore, previously reduced by a gas such as water gas. The water gas process involves passing water gas and steam over a catalyst at elevated temperature; the carbon monoxide reacts with the steam to form hydrogen and carbon dioxide, the latter being removed by suitable absorption methods. It is particularly useful where hydrocarbons are not available.

The general tendency in modern plants which have access to hydrocarbons such as natural gas, refinery gases, or liquefied petroleum gases is to use the hydrocarbon-steam process developed by Girdler (5A). In this process, purified hydrocarbons are catalytically reformed with steam at high temperature to produce carbon monoxide, carbon dioxide, and hydrogen, and the carbon monoxide is further converted to carbon dioxide by adding more steam and passing the mixture over a second catalyst in a manner similar to the water gas process. Carbon dioxide is removed by absorption in monoethanolamine solution. Residual carbon monoxide is removed either by further conversion or by a combination of conversion and methanation. The latter scheme is employed in Mrs. Tucker's plant.

Mrs. Tucker's started with a steam-iron unit in 1935. In 1942 Girdler added carbon monoxide conversion in order to increase the purity of the steam-iron hydrogen, and monoethanolamine absorption for carbon dioxide removal was later installed. The present hydrocarbon-steam plant was built in 1947 to replace the steam-iron unit. The raw gas produced by the hydrocarbon-steam reforming was employed as the reducing gas in the steam-iron generators for several months while the purification section of the new hydrogen plant was being completed.

General operation of Girdler units using propane has been covered in the literature (9, 20), but specific plant units have not been described. The unit at Mrs. Tucker's, using natural gas both as fuel and process feed and employing the methanation step for final purification, is considered to be one of the most advanced of the Girdler installations. This unit has a rated capacity of 12,500 cubic feet of high purity hydrogen per hour.

Natural gas consisting of about 85% methane, 11% ethane, and 4% nitrogen is compressed at the rate of 6000 cubic feet per hour to 35 pounds per square inch gage pressure for use as process feed and furnace fuel. Approximately one half of the natural gas is used for fuel. Before it enters the reformer furnace, the process feed gas is passed through activated carbon drums for the removal of residual sulfur compounds or odorants, such as mercaptans, which may have been added to the gas. Removal of sulfur compounds is desirable to protect the nickel catalyst used in the reformer. The activated carbon is periodically regenerated with steam. When a relatively high concentra-

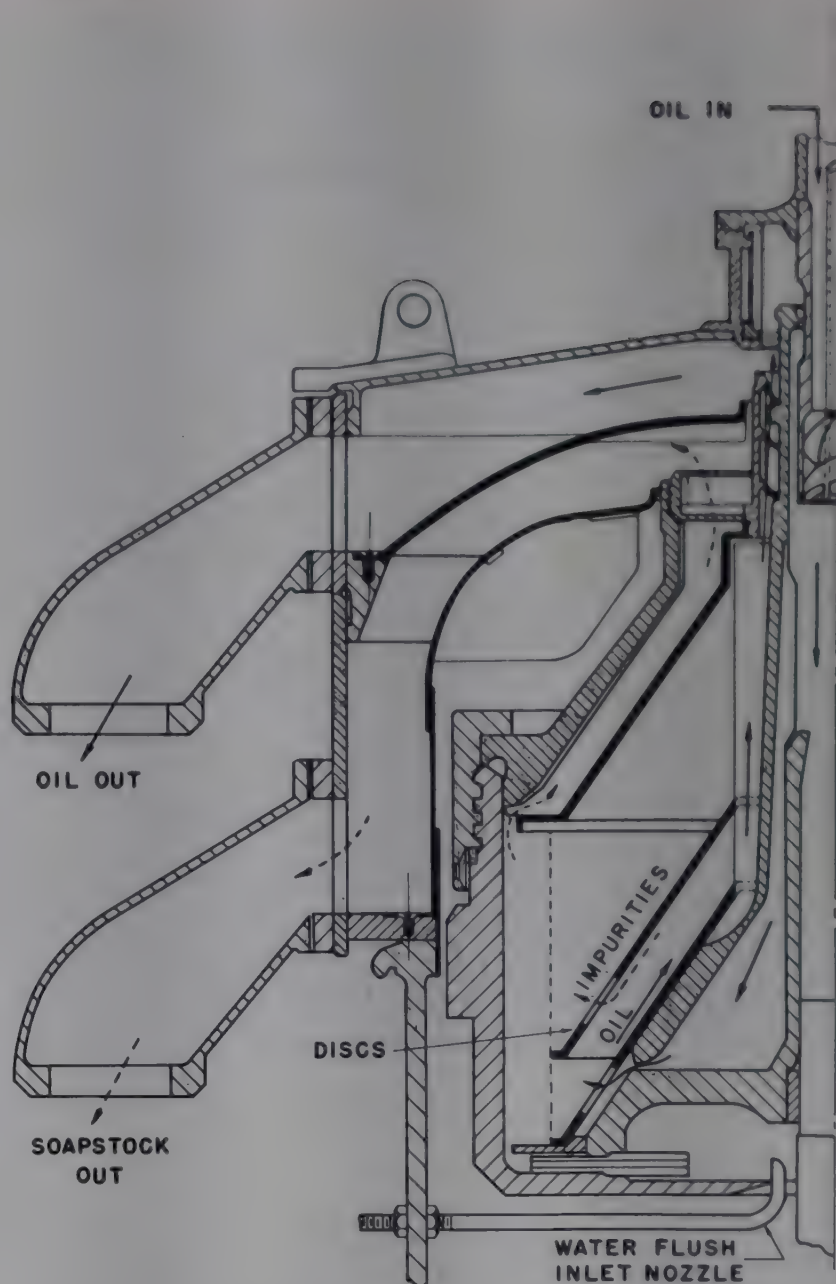


Figure 4. Cross Section of Re-refine Separator

tion of sulfur compounds is present in the process feed, other means of sulfur removal may be used, such as conversion of the organic sulfur compounds to hydrogen sulfide and absorption of the hydrogen sulfide into caustic or monoethanolamine solution. Natural gas supplied to plants in north Texas, however, does not require this special treatment for sulfur removal.

The reformer furnace is a vertical refractory-lined steel structure. Alloy steel tubes, approximately 30 feet long, are suspended in the furnace and extend through openings in the arch and hearth of the furnace. The tubes are charged with a nickel-base catalyst resting on grid supports mounted near the bottom of the tubes. The furnace is fired by multiple burners arranged in a vertical plane along the shell of the furnace. A coil mounted in the flue gas outlet at the top of the furnace is used to superheat some of the steam required for the reforming and carbon monoxide conversion steps.

In operation, superheated steam and process natural gas enter a mixing header, and the mixture is delivered to the top of the reforming tubes and distributed to ensure substantially uniform feed rates through the different tubes. The reaction mixture is heated to approximately 1500° F. in its passage through the tubes, where the following reactions take place:



The methane and other hydrocarbons are almost completely reacted, so that the raw gas at the outlet of the reformer furnace contains only about 1% of inert material which is essentially all nitrogen. This hot gas, consisting of roughly 16.5% carbon monoxide, 7.0% carbon dioxide, and 75.5% hydrogen, is cooled to about 700° F. by the addition of steam and then passes to the

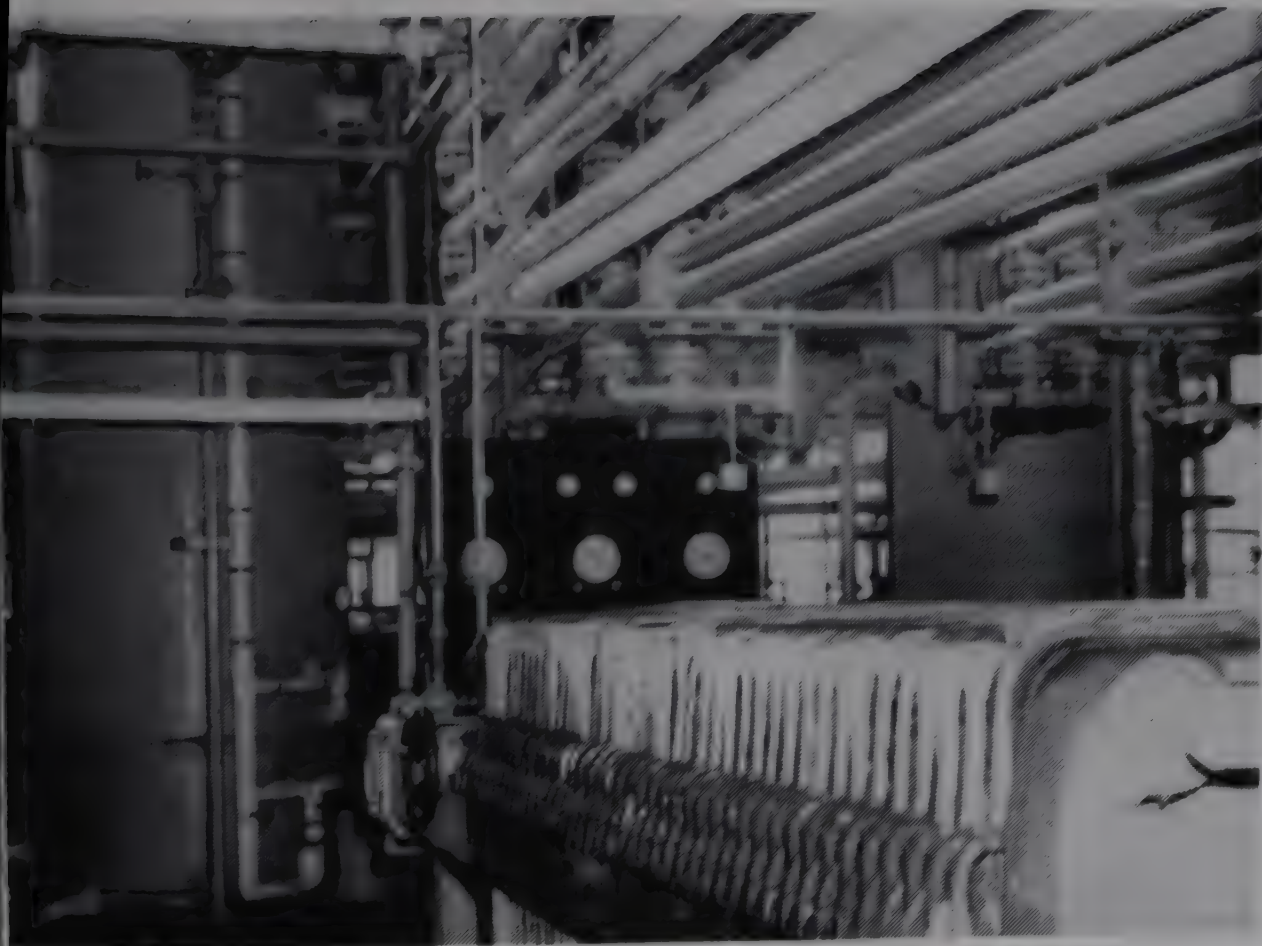


Figure 5. Vacuum Bleaching Towers

first-stage carbon monoxide converter. This converter is a vertical vessel, containing a pelleted iron-chromium conversion catalyst; the following reaction takes place:



The composition of the process gas as it leaves the first-stage converter is approximately 1.0% carbon monoxide, 19.5% carbon dioxide, and 78.5% hydrogen. After cooling, the gas is ready for the first stage of carbon dioxide removal. Coming from the top of the first-stage converter at about 725° F., the gas passes through the shell side of a heat exchanger in which it is cooled to about 500° F. and then through a water cooler where it is cooled to about 100° F.; it then flows into the bottom of the first-stage carbon dioxide absorber tower. Aqueous monoethanolamine solution from the second-stage absorber flows down through the tower absorbing carbon dioxide according to the following equations:



The gas from the top of the first-stage absorber is substantially all hydrogen (97.4%) with the carbon dioxide content reduced from almost 20% to less than 0.5%, but the carbon monoxide content (1.25%) is still considered quite high.

A second-stage conversion and absorption will remove all but about 0.1% of this carbon monoxide and produce a hydrogen product of about 98.6% purity. In order to heat the gas to reaction temperature for the second conversion, it is first passed through the tube side of the heat exchanger used for cooling the gas from the first-stage converter, and the proper quantity of superheated steam is then bled into the line leading to the second-stage converter. Gas from the top of this converter passes through a second heat exchanger and a water cooler where the temperature is again reduced to about 100° F. for the second-stage absorption step. Monoethanolamine solution for this absorption step comes from the regeneration coolers.

Girdler hydrogen units ordinarily have a third conversion and absorption step, but the unit at Mrs. Tucker's employs a methanation step rather than further conversion. This is economical from the standpoint of steam consumption and equipment required. Gas from the top of the second-stage absorber passes

back through the second-stage heat exchanger where it is heated to about 525° F. by the gas from the second-stage converter. The gas then enters the methanator, which is a drum containing a nickel-base catalyst, where the following reactions take place:



The gas leaving the methanation stage is high purity hydrogen containing less than 0.01% each of carbon monoxide and carbon dioxide. The only other impurity of any consequence is the inert nitrogen present in the original natural gas.

The rich monoethanolamine solution is continuously regenerated, first flowing from the bottom of the first-stage absorber through a heat exchanger where it is heated by lean solution returning from the reactivator. The rich solution then passes to the top of the reactivator, and as it flows down through the tower, it is heated and stripped by steam rising from the re-

boiler mounted at the base of the tower. At the boiling temperature of the solution, the amine salts dissociate, releasing carbon dioxide which is swept from the top of the reactivator by the rising steam. This carbon dioxide is cooled after it leaves the reactivator to permit recovery of the steam; it is then discharged to the atmosphere. The lean amine solution flows from the base of the reactivator back through the solution heat exchanger previously mentioned, then through a water cooler, and finally is pumped to the top of the second-stage absorber.

Reaction. The nickel catalyst is put into a 1000-pound tank containing enough hot oil to melt it. The usual quantity of catalyst is 50 pounds, with a like quantity of filter aid (2A) added to facilitate removal of the catalyst after hydrogenation.

Mild steel hydrogenators or converters (Figure 6) are used; each holds 29,000 pounds. These are equipped with coils through which either water or steam may be piped and are agitated at 120 to 170 r.p.m. Hydrogenation is a batch process; the converters are filled to 90% of capacity with the oil, which is heated to drive off any moisture that might be present. The hot catalyst is then pumped in and mixed thoroughly with the oil. Hydrogen is bubbled in at the bottom through a perforated ring and pipe distributor; the rate of admission is controlled by a pressure reducing valve. Because inert gases and unabsorbed hydrogen accumulate during the process at the top of the converter and the pressure increase would normally cause the hydrogen feed to be eventually cut off, a means of continuously bleeding off these gases is provided. This mixture, called revert hydrogen, is returned to the hydrogen unit, and the flow control valves on the converter, governing this return, are adjusted manually. Further, each converter is equipped with relief valves, which open at 90 pounds per square inch pressure and discharge to the atmosphere.

A typical hydrogenation curve is shown in the title figure of this paper. The process is carried out for a period of 1 to 1.5 hours, at a temperature of 330° to 340° F. and pressures of less than 25 pounds per square inch (Figure 7). A minimum pressure of 5 pounds per square inch is maintained at all times, and each of the converters is equipped with recording thermometers and recording pressure gages. Weighted averages at Mrs. Tucker's show a consumption of 0.604 cubic foot of hydrogen per pound of oil hydrogenated.

A number of European plants are reported (16) to use a

circulating system, in which the hot oil is continuously circulated from the bottom to the top of the kettle during hydrogenation. The continuous method of Bolton (8) has also been used in several plants in Europe, but it is understood that the English owners of this process, Technical Research Works, are not at present promoting it to any degree. In this method the catalyst, consisting of nickel turnings or wire, is held in a wire basket nearly filling the hydrogenator. Warmed oil enters the top; hydrogen gas enters the bottom and is circulated through the hydrogenator. The degree of hydrogenation can be controlled by altering the rate of oil flow. One advantage claimed for this process is an improved pale color due to the short period of heating. Some developmental work on this process is understood to have been done on the West Coast, but no commercial units have as yet been erected in this country.

Referring again to the question of partial hydrogenation, Wurster (30) clearly defines the difficulty in hydrogenating edible oils to shortenings and other products when he says that the problem resolves itself into a proper control of the operating conditions so as to obtain as high an olein content as possible by converting the less saturated esters to olein, without formation of the esters of completely saturated acids and iso-oleic acid. Mrs. Tucker's Foods attempts, as does the rest of industry generally, to obtain an oil of the lowest iodine number (and therefore the least unsaturation) compatible with a relatively low melting point. The quantity of hydrogen involved in accomplishing this will depend not only on the oil being hardened and the degree of hardness desired, but also on the tightness of the equipment and the purity of the hydrogen. Using normal methods of determining degree of hardness (1), the desired end point would be passed over long before the operator was advised of the results. Therefore a quick test on the operating floor is necessary. For this purpose the operator uses the butyro refractometer scale, which has been closely correlated with the iodine value. This test requires only about two drops of oil from a convenient sample cock and is finished in 3 minutes. In an emergency the operator is allowed to drop the batch on this test alone; normally, however, it is confirmed by a cloud point test in the laboratory.

After the oil has been hydrogenated to the desired point and the results confirmed by the laboratory, it is cooled to 200° F. to avoid oxidation during filtering and discharged into one of four dropping kettles. From the kettles it is steam-pumped to open-discharge type plate-and-frame filters, where the catalyst and filter aid are removed.

Although the oil has usually been bleached prior to hydrogenation, a posthydrogenation bleach (postbleach in plant terminology) is necessary. This bleach removes the greenish cast of the oil, whereas the main bleaching operations removed primarily the red color. Bleaching clay (0.5 to 0.6% of the oil by weight) is added, and the oil is put through the regular bleaching process at 220° F. Here both batch bleaching equipment and the equipment used to develop the continuous bleaching system are employed. After the postbleach the oil is again filtered, this time through two closed-discharge type plate-and-frame filters operated in series. An additional filter serves as a cleanup filter. The closed type discharge is required for these filters because air must be excluded.

The only time hydrogenation is carried to completion is when stearin is desired. This fully hydrogenated fat is normally used in shortening formulations, but if it is to be sold as stearin it is flaked on a refrigerated steel cylinder, or chill roll.

Returning to the catalyst, it is customary in some plants to allow the catalyst to accumulate to the capacity of the filtering equipment and then to hold this amount substantially constant by discarding a fraction after each run and adding an equivalent fresh portion of catalyst for the next run.

Economy requires that nickel catalyst be used for as many cycles of hydrogenation as possible. However, on repeated use, catalyst gradually loses both activity and selectivity. Since

oils of a wide variety of specifications requiring differing degrees of catalyst activity are produced in this plant, opportunity is afforded for optimum catalyst utilization.

To accomplish this Mrs. Tucker's Foods grades catalyst into four grades, depending on its ability to hydrogenate oils to certain set specifications. The No. 1 grade is assigned to fresh catalyst, No. 2 and 3 to intermediate grades, and No. 4 to the least active grade. The latter is used exclusively for the production of completely hardened oil, or stearin, since selectivity of hydrogenation is not required for this use. After use for stearin hydrogenation, activity is so reduced that the catalyst is useless for practical purposes, and it is discarded.

A catalyst concentration of 0.02 to 0.05% of nickel content based on the weight of the oil is commonly used in hydrogenation. By proper choice of catalyst grade and quantity, together with proper temperature and pressure conditions, all of which affect the course of the hydrogenation reaction, fats to meet the requirements of most commercial uses are produced by varying the degree of reduction of the unsaturates in the oil.

DEODORIZATION

Bailey (4) says that one reason for the general practice of deodorizing vegetable oils in this country is the general unfamiliarity of the people with natural oil odors and flavors, and a



Figure 6. Hydrogenation Converter

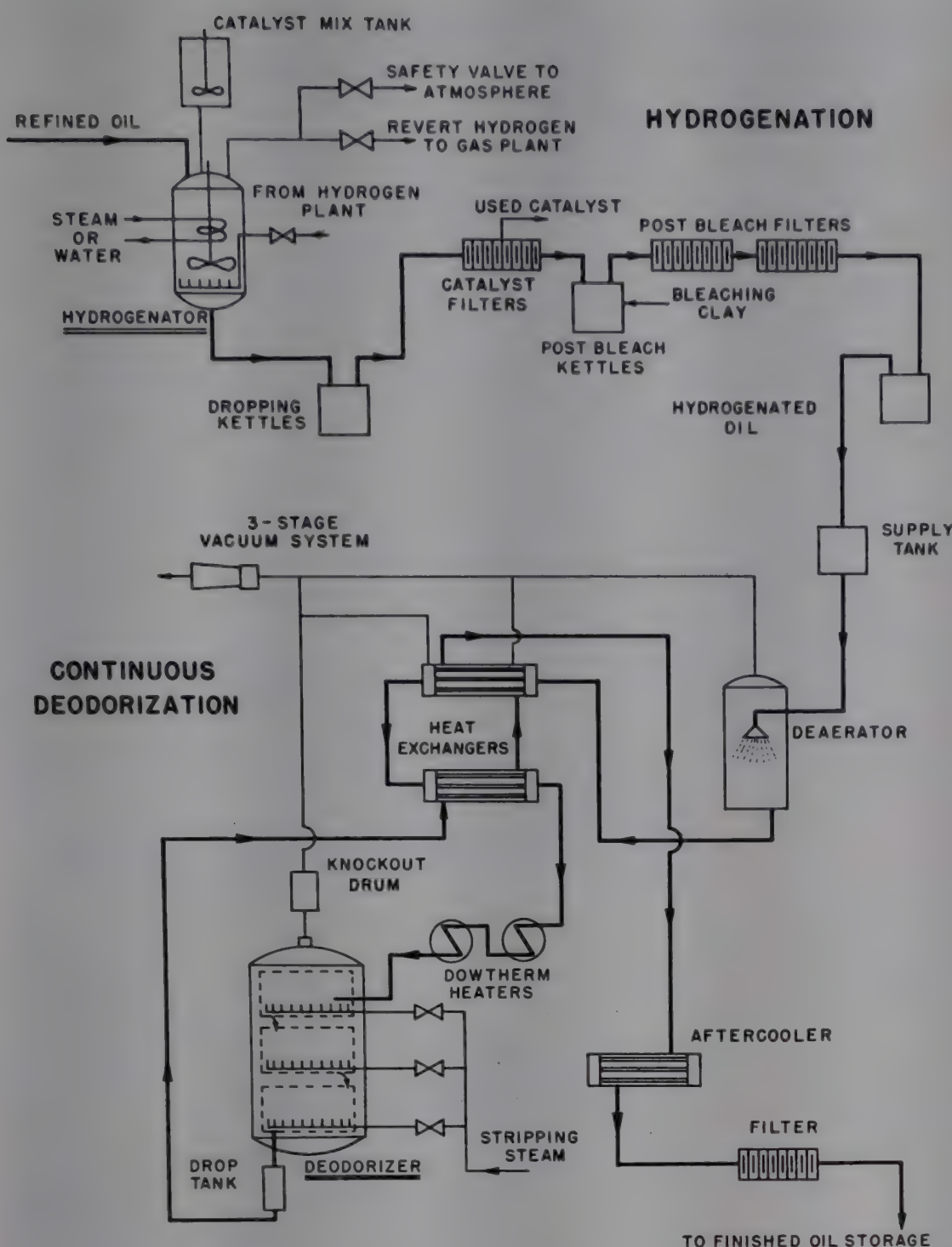


Figure 7. Flow Sheet of Hydrogenation and Deodorization Processes at Sherman, Tex., Plant of Mrs. Tucker's Foods, Incorporated

second reason is that methods of extraction of the oil and the scale on which we extract it more often lead to odoriferous materials than do Oriental methods. Raw cottonseed oil, at least, is very strongly and unpleasantly flavored, and must be processed for flavor removal before it is considered edible in this country.

Not only is the problem of undesirable odor and flavor a very important one, but it is also a complicated one in that different materials apparently give rise to varied flavors and odors depending on whether the oil is raw, refined, or made into finished products. Regarding the raw oil, Davidsohn and Davidsohn (12) state that unpleasant flavor and odor are due primarily to fatty acids liberated during different stages of rancidity development, and that they are generally low molecular weight compounds, oxy- and keto-fatty acids, which are readily removed by the alkali treatment which the oil undergoes in the refining process. They point out, however, that some of the phosphatides present in the raw oil are themselves natural stabilizers and their destruction in the refining process gives rise to rancidity and odors. Bailey (3) agrees that the constituents causing the odors are probably aldehydic or ketonic in nature, and adds that even hydrogenation of a previously odorless and colorless oil results in a characteristic flavoring whose identity is as yet unknown. He feels, however, that the odor and flavors ordinarily removed in deodorization have nothing to do with rancidity. He also points

out that the concentration of the odoriferous substance is ordinarily less than 0.2%. A generally accepted view of the origin of the odors is held by Robinson and Black (21), who say that the odor and flavor of raw cottonseed, soybean, and peanut oils are due apparently not to the glyceride structure, but to "foreign" ingredients originating in the fruit, husks, or seed from which the oil is expressed. Some of these foreign ingredients may be aldehydic or ketonic in origin. Recent analyses of deodorizer distillates have been made by Jasperson and Jones (17).

Regardless of the source or nature of the odors it is necessary that they be removed, and this is accomplished by what is essentially steam distillation at reduced pressures. This may be done either batchwise, or by the new continuous methods, and both of these techniques are employed at Mrs. Tucker's plant. Steam deodorization probably originated in France, and European plants have used it for many years for production of margarine oils.

With either the batch or continuous processes there are a number of problems involved (3) which bear careful watching. For efficient deodorization, the oil must be processed at a high temperature, and a high vacuum must be maintained to assist stripping and to avoid hydrolysis of the oil by the stripping steam. To protect the color and stability of the oil and ensure good flavor and odor, there must be rigorous exclusion of air from the hot oil, either as leakage into the deodorizer or as present in the stripping steam. At very high temperatures there is a substantial loss of material other than free fatty acids distilled from the oil. A sub-

stantial part of this consists of sterols and other unsaponifiable material, and it has been thought that the remainder consisted of triglycerides. Recently published data (18) on the vapor pressure of the pure triglycerides indicate, however, that a substantial loss of oil in the form of triglycerides is impossible, hence it may be that the fatty material distilling over consists of mono- and diglycerides. Losses of oil by entrainment tend to occur with excessive rates of steam flow. Figure 8 shows the effect of steam flow on such losses in continuous deodorization. Bailey in a recent article (5) discusses another system, the semi-continuous, and compares its advantage with the other two methods.

Batch Deodorization. Formerly it was difficult to attain the high temperatures required in deodorization: special high flash point heating oil or high pressure steam (600 pounds per square inch) was used in coils in the still. In other systems the vegetable oil was circulated through coils extending into a furnace. In the last few years the problem has been very much simplified by the use of Dowtherm as a heating medium. The batch system used at Mrs. Tucker's consists of mild steel tanks, 8 feet in diameter and 12 feet high. The oil is pumped into these tanks to a depth of about 6 feet and raised to approximately 450° F. by condensing Dowtherm vapor at 500° to 525° F. in coils in the tanks.

The batch is then steam-distilled for a period of 4 to 5 hours,

using superheated (450° F.) steam introduced into the bottom of each vessel through a distributor. The quality of the stripping steam is watched closely to control any possible reaction between the iron of the vessel and the stripping steam. After deodorization is complete, water is passed through coils in the deodorizers to cool the oil to 275° F. The oil is then dropped into one of four cooling tanks (two 60,000 pounds each; two 40,000 pounds each) where it is cooled under a vacuum of about 29 inches of mercury. The batch technique is carried out at 8 mm. of mercury absolute pressure, using a three-stage ejector. The size of the vacuum unit, considerably greater than that necessary in continuous deodorization, is shown in Figure 9.

Continuous Deodorization. The continuous deodorization system (5A) has a number of advantages over the batch technique, although it is not quite so flexible (Figure 9). Steam required for the actual stripping is about 25% of that required by the batch method, and since a small vacuum system is necessary, less steam is needed to drive the ejectors. Routine stripping steam requirements on the continuous system amount to approximately 0.03 pound and ejector steam to 0.11 pound, per pound of oil. Over-all steam consumption per pound of finished oil, for batch and continuous systems combined, amounted in 1949 to 0.778 pound. This figure included losses, line leakage, ejector operation during times of no production, and rerunning stock. Oil handling problems are easier and the stripping efficiency is much higher with the continuous system than with the batch method because of better contact of stripping steam with the oil. (Most deodorization in the batch method takes place on the surface of the oil.) Further, considerable heat is saved by the use of economizers. Distillation and entrainment degradations with the batch method (0.6%) are three times that of the continuous system.

The continuous system consists of one mild steel vessel 8 feet in diameter, containing three nickelclad trays 21 inches high on which the oil flows at a depth of 9 inches. The trays are baffled and the oil flows from the top tray downward. Steam is introduced into each tray with separate distributors to each baffled section in the tray, and there is a free space between the trays and the vessel walls into which the stripping steam discharges after it leaves the oil. This prevents air which may accidentally leak into the vessel from coming into contact with

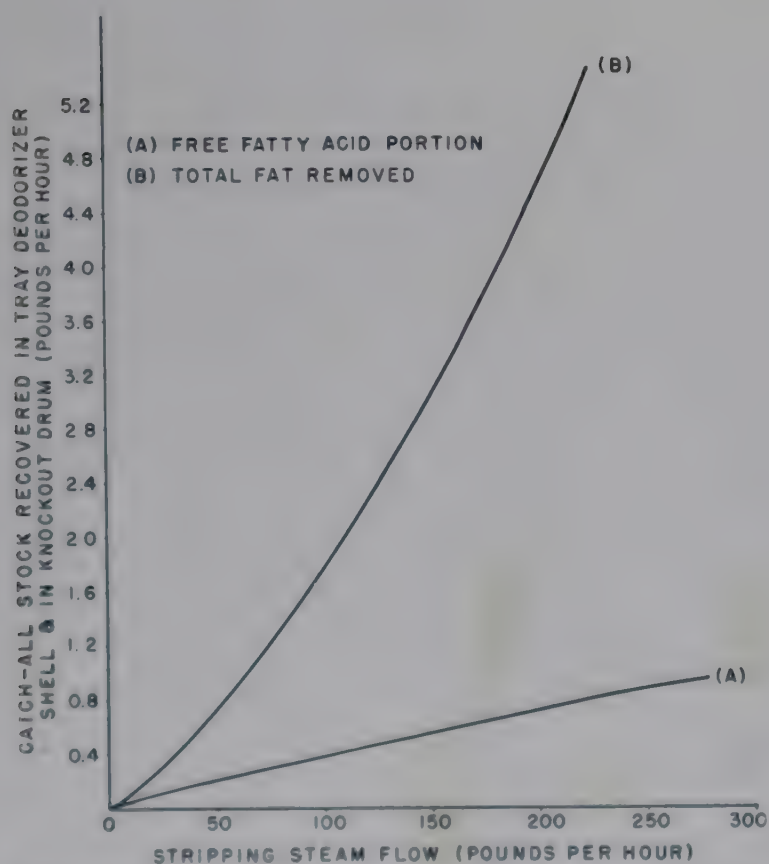


Figure 8. Effect of Steam Flow on Distillation and Entrainment Losses in Continuous Deodorization

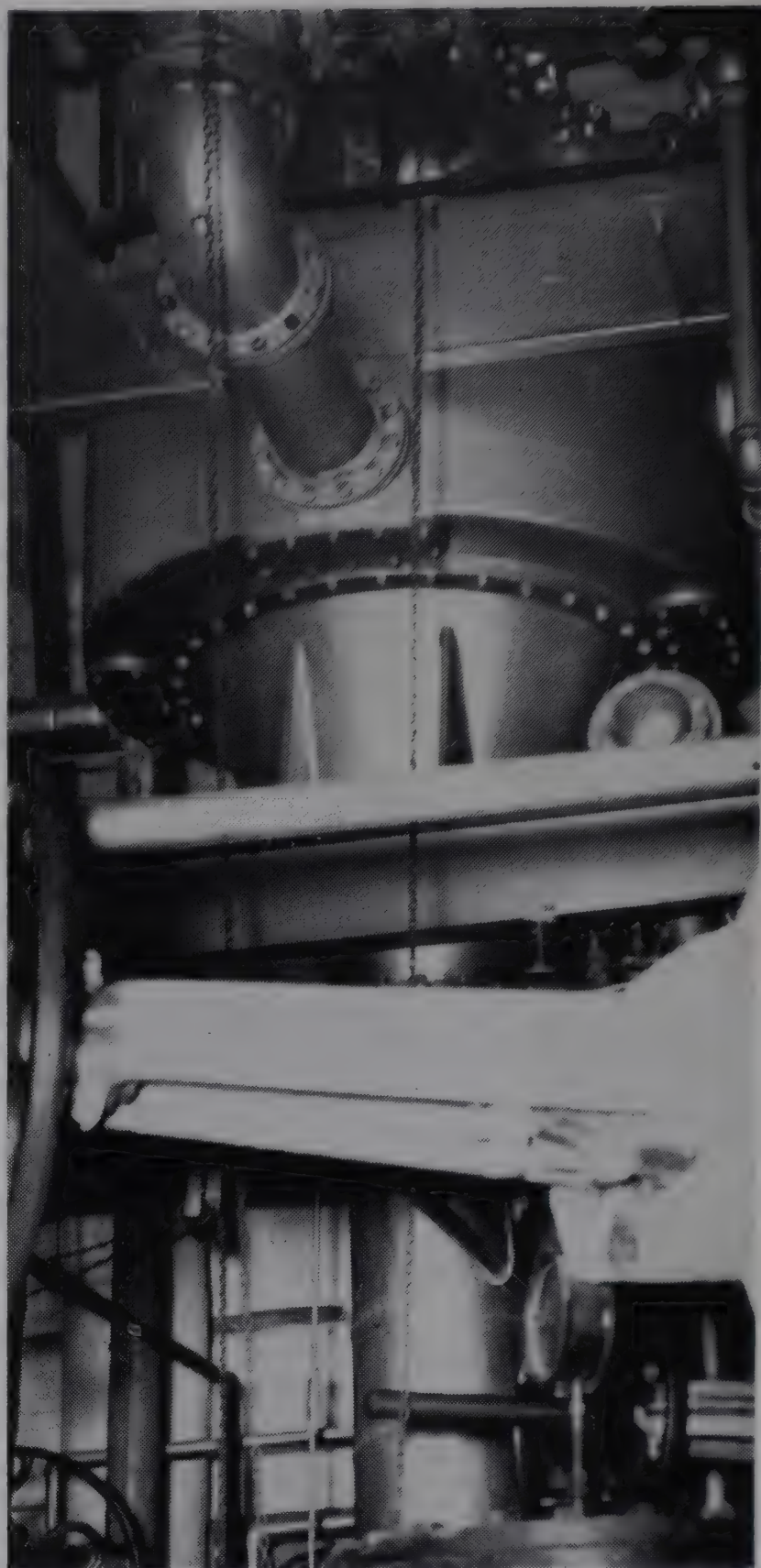


Figure 9. Top of Batch Deodorizer Indicates Size of Vacuum Equipment Required for Batch Deodorization

the hot oil. All piping used where temperatures are in excess of 200° F. is either nickelclad, Type 316 stainless steel, or aluminum.

The system is under 4 mm. of mercury absolute pressure, using three-stage steam jet ejectors. The oil is first pumped into a deaerator where it is flashed at 4 mm., with a retention time of approximately 3 minutes. It then passes through the tube side of aluminum economizers where it is preheated by oil leaving the system and is further heated to 450° to 475° F. in Dowtherm heat exchangers, using Dowtherm A. From these exchangers it is fed into the top tray of the deodorizer. Total retention time in all three trays is about 54 minutes. The deodorized oil drops by gravity into a surge tank, is then pumped through the shell side of the economizer previously mentioned, and finally through the shell side of an aluminum water cooler. It is then filtered and goes into the finished oil tank. A knockout drum at the top of the vessel, in the vapor line to the ejectors, takes care of condensed fatty acids and odoriferous material including tocopherol. Other fatty acids are collected at the bottom of the vessel housing the trays and drain into a knockout drum.

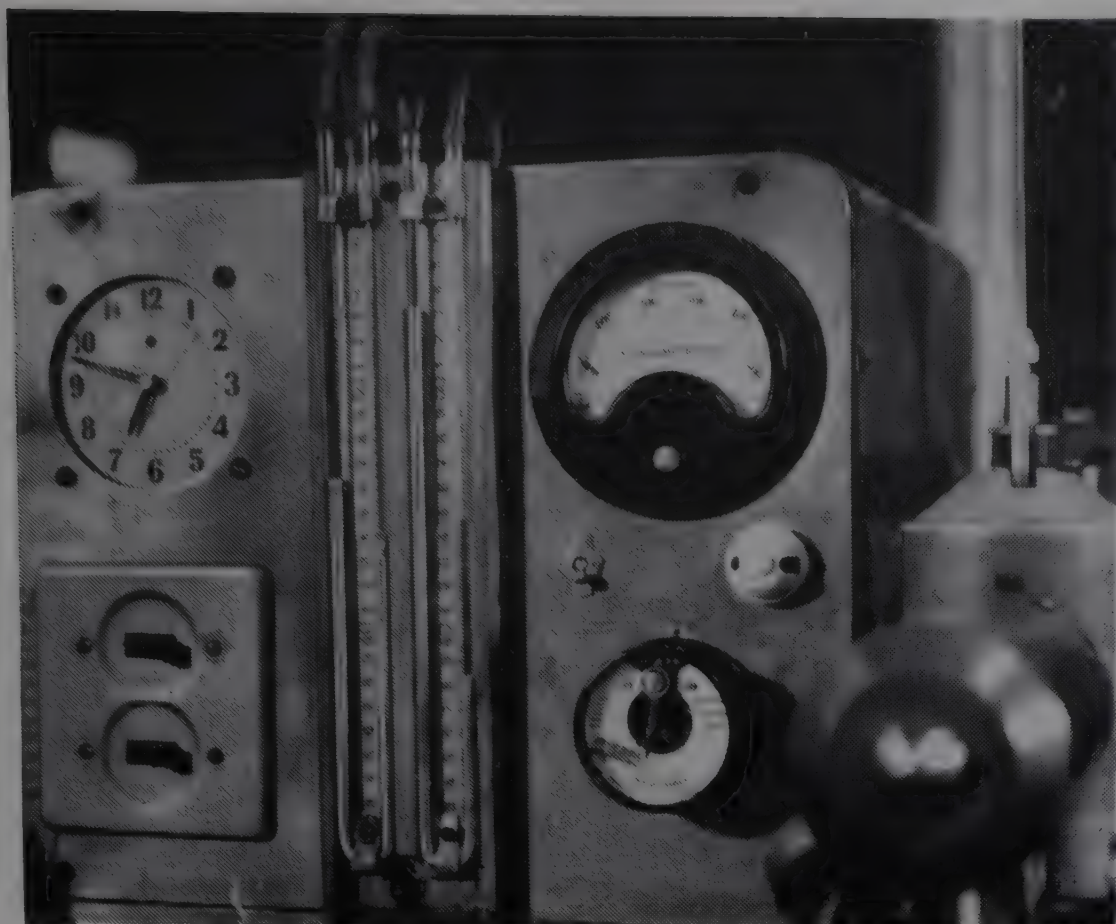


Figure 10. Cloud Point Apparatus

PACKAGING

The term packaging, as used in vegetable oil processing, differs somewhat from that ordinarily employed in industry in that it not only involves putting the finished product into packages but also the preparation for that step, including, in the case of margarine, the blending of the component materials into the finished product.

The history of the use of vegetable oils in shortenings, first as adulterants for lard shortenings and in the past generation, because of development of catalytic hydrogenation, in all-vegetable oil shortenings, has been discussed by Slaughter (22). Demands for uniformity in consistency, texture, and color have seen the production of shortenings develop through the stages of crystallization in agitated, water-jacketed tanks and use of the internally refrigerated chill roll to the closed, continuous internal chiller and plasticizer.

Shortening. Shortening base from the hydrogenation step may be modified into one of four types of shortening before being deodorized and then packaged. Standard shortening consists of a mixture of 60-titer stearin (titer is the measure in °C. of the temperature of solidification of the fatty acids), oil partially hydrogenated to a definite end point, and soft or unhydrogenated oil. This type shortening is easy to handle over a wide range of temperature. Hydrogenated shortening consists entirely of hydrogenated oil and emulsifier-type shortening has superglycerinated fat added. Superglycerinated oils are merely oils with a high proportion of monoglycerides rather than triglycerides, and these when added to shortening improve the emulsifying properties. The fourth type shortening is termed colloquially B & C or "biscuits and crackers"; it is to be employed in baking products which must have long shelf life, and to ensure stability this shortening is hydrogenated to a very low linoleic acid content.

Whatever the nature of the modified base, it is transferred from the storage tanks to a water-jacketed precooler, where it is cooled to about 110° to 115° F. and aerated by inert gas drawn through a calibrated valve on the suction side of the pump to the precooler. It is then chilled rapidly in a continuous closed unit (5A), which because of high ratio of surface area to volume (8.5 square feet of heat transfer area; 22 pounds of fat per tube at any instant) affords excellent heat transfer and which also mixes the shortening thoroughly during cooling. This unit

consists essentially of an ammonia-refrigerated tube having a shaft rotating inside at 500 r.p.m.; the size of the shaft is such that a narrow annular passage is left between it and the tube. The product is pumped through this passage where chilling and crystallization take place in a few seconds. Floating scraper blades are attached to the shaft and are held against the wall of the refrigerated tube by centrifugal force. These continuously remove the crystallized film and allow the high heat transfer rate to be maintained. The supercooled and partially crystallized shortening is then pumped to the plasticizing and tempering unit where it is "creamed" or "picked" by means of spiral rotating fingers intermeshing with stationary fingers. This creaming allows partial liberation of the heat of crystallization with formation of a plastic solid from the supercooled liquid.

The product is forced at a constant and comparatively high pressure (300 to 400 pounds per square inch) through the chilling and plasticizing units. It is then delivered through an atomizing orifice directly into the package. (Filling machines are of the positive displacement, volumetric type.) The pressure release through the atomizing orifice also allows the 10 to 12% air, which is for the most part in solution at the higher pressure, to come out of solution. This, combined with further fine division of the air bubbles by liquid shear, results in the characteristic white coloring of the shortening. After packaging the shortening is "tempered" or held at a controlled temperature (80° F.) for 2 or 3 days until the crystalline structure of the shortening becomes stabilized.

Margarine. Margarine was introduced in France in 1870, and up to a few years ago it was made batchwise by the so-called wet or ice-water crystallizing method. It is made from pasteurized skim milk and vegetable oil, fortified with vitamin A; government specifications (27) require a minimum of 80% fat, approximately 16% water, 2 to 3% salt, and 1% nonfat milk solids. Cultured milk and salt from a blending tank are added to a mixture of the margarine base oil containing vitamin A concentrate, coloring matter if desired, and lecithin, which acts as an antisticking and antispattering agent and to some extent as an emulsifier. Other emulsifiers, such as monoglycerides, may be added. The mixing is done without further addition of

TABLE II. LABORATORY CONTROL TESTS

Test	Oil				Finished Product
	Crude	Refined	Undeodorized	Deodorized	
Refining loss	X
Flash point	X
Moisture	X	X
Bleach	X	X
Color	X	X	X	X	X
Free fatty acids	X	X	X	X	X
Soap content ^a	..	X
Refractive index ^a	..	X	X
Flavor and odor ^b	..	X	..	X	X
Titer	X	X	..
Cloud point ^a	X	X	X
Wiley melting point	X	X	X
Iodine value	..	X	X	X	X
Cold test	X	X	X
Visible impurities	X	X	X
Filterable impurities	X	X	X
Congealing point ^a	X	X
Peroxide number ^a	X	X
Swift stability ^a	X	X
Penetration ^a	X
Per cent air ^a	X
Vascelation time ^a (at 90° F.)	X

^a Not an official or tentative method of A.O.C.S.

^b To detect presence of musty or unfavorable odor.

heat and the loose emulsion is then ready for chilling and packaging.

The chilling of margarine is done in the *A* unit, a series of three tubes (capacity 4500 pounds per hour) similar to that used for chilling shortening, except that, because of the corrosiveness of the emulsion, the heat transfer tubes are made of pure nickel and all interconnecting piping is stainless steel. After being chilled to 50° F., the supercooled fluid goes into the *B* unit, where it is slowly forced through a 7-inch tube, without agitation. Here it slowly solidifies with a temperature rise to about 70° F., and the plastic solid is formed. It is then delivered to the automatic machines for "working," forming, and wrapping of the prints. Slaughter (22) calls attention to the fact that the European method is radically different, involving feeding the liquid emulsion onto a chill roll, then through working rolls, and finally through a slab cutter. The Europeans claim that their product more nearly resembles butter.

For both shortening and margarine the closed continuous system provides almost completely automatic operation, considerable saving in labor (two to three times the quantity with half the labor), uniformity, and extreme cleanliness. There is also a great saving in the time required for production of finished margarine, since only about 5 minutes are required from emulsion to packaged margarine with the new methods as compared with the older methods which required from 1 to 3 days.

LABORATORY CONTROL

The entire operations of the plant are covered thoroughly by the laboratory from the standpoint of routine control. Table II gives the tests made on the material at each stage of the operations.

Since consistency is one of the most important characteristics in shortenings and margarines, it must have careful tests in this regard. The quick butyro refractometer test by the operator in the hydrogenation step has already been discussed, and mention was made of a laboratory follow-up with the cloud point

test. This is considered the most important test which the laboratory has to make. The laboratory at Mrs. Tucker's Foods has correlated this strictly empirical test against common consistency controls (Wiley melting point and iodine value) and is able to bring the product to a predetermined consistency—that is, to stop the hydrogenation at a particular endpoint—by means of the cloud point value. This development has proved valuable from the standpoint of time also, as the cloud point test takes a maximum of 15 minutes to perform, varying somewhat with the hardness of the oil being tested.

Cloud point equipment (Figure 10) consists of a cooling chamber, a light source, a photoelectric cell, and a microammeter, all mounted on a cabinet in which refrigerated water is continuously circulated. The cooling chamber is of brass and is mounted between light source and photoelectric cell. The sample, heated to slightly above 60° C., is put in a beaker similar to a 180-cc. electrolytic beaker and placed in the cooling chamber. Cold water, circulating to cool the sample at a predetermined definite rate, impinges on screens on opposite sides of the beaker and runs down the screens and the side of the beaker. A motor-driven agitator is placed in the oil, carrying with it a thermometer whose bulb is placed approximately in the center of the sample. Cooling is carried on until the sample is at 50° C., at which time the light source is adjusted so that the microammeter reads 300. The light source is then transmitting 120 foot-candles of light through the oil sample. The sample continues to cool, and a Sensitrol relay causes a buzzer to go off when the ammeter reading is 50 microamperes. At this point the sample has clouded so that transmitted light is equivalent to 20 foot-candles. Temperature is then read from the thermometer. Cloud point is defined as the temperature in degrees centigrade at which crystallization has occurred to such an extent that it reduces the light transmitted through the oil sample from 120 foot-candles, at 50° C., to 20 foot-candles. A continuous check of control on shortening and margarine is maintained by penetration tests over a wide range of temperatures, employing a special cone-shaped needle in a conventional penetrometer.



Packaging Margarine Prints

FUTURE PROSPECTS

Improvements are to be expected in the extraction of oils, guaranteeing better quality oil, and it is expected also that the problems in solvent extraction with trichloroethylene will be ironed out so that hydrogenators can use oil made by these methods without fear of poisoning their catalysts. In the future a considerable amount of rice bran oil will probably be extracted and processed as a good grade oil.

In refining processes the industry is most interested in reduction of oil losses and in improvements in continuous refining processes. Pilot plants are in operation employing liquid-liquid extraction in refining, instead of the addition of chemicals to saponify the fatty acids. It is possible that in the foreseeable future even the soda ash process will become obsolete. Further, industry is looking for methods for recovering and separating the potentially valuable materials contained in the foots from alkali refining.

Weir (29), discussing the bleaching agents—air-bleaching with cobalt borate catalyst, and chrome-bleaching with sodium dichromate and sulfuric acid—used in preparing fats for soaps, points out that although fuller's earth for bleaching has largely superseded chrome-bleaching, it has the definite disadvantage that the press cake contains a large amount of oil which cannot be entirely removed except by steaming. That is equally applicable to edible oils, and Mrs. Tucker's research laboratory is currently working on a process for recovery of this oil. Major obstacle is the development of additional undesirable color. It is also possible that industry will find a method of separating some of the concentrated impurities from the bleaching process. Of particular interest in this case is the concentration of carotene from the bleaching of soybean oil.

Hydrogenation badly needs a continuous process. The main difficulty here lies in control of selectivity; this is a big problem because no matter how well the oil is bleached, it still contains a certain amount of impurities which will poison the catalyst. Some method perhaps similar to the Bolton method already mentioned, with modifications to produce a material acceptable by American standards, may be forthcoming.

Deodorization is a substantially well developed technique, but the recovery of concentrated odoriferous materials from the knockout drums should be of interest. Crude tocopherols, sources of vitamin E, and already mentioned, are an example.

Packaging units have been developed to a very efficient state, but crystallization problems are still important. The shortening is supercooled and crystallizes into small crystals which are interlocked. The picker breaks up these crystals, allowing a greater degree of hydrogenation during that step without unsatisfactory consistency in the final product. If the shortening could be allowed to cool slowly, with the formation of large crystals, and these crystals could then be broken up by some sort of homogenizer, a considerable forward step would be made. Work is being done in industry toward improving the manufacture of emulsifiers—for example, the monoglycerides—particularly in the direction of a continuous process.

Lastly, there is a need for the development of a continuous process for winterizing salad oil. No satisfactory centrifuge has been found for separating out the materials which crystallize during this process. Preliminary work on winterizing salad oil in a solvent was reported by Bailey (?) in 1943. Subsequent work, unpublished, has shown that a superior salad oil could be produced by solvent crystallization with reduction in the time allowed for crystallization and crystal growth to about 1 to 1.5 hours. There appears to be no doubt that a continuous installation using this process is practicable, providing that the plant could be made large enough to justify the rather large capital expenditures for continuous closed filters, solvent recovery equipment, and safety devices. The main difficulty along this line appears to lie in the fact that possibilities for effecting improvements in conventional processes for treating oils and fats are limited by the relatively

small production of fatty oil products, in comparison with other products, and the widely scattered existing production facilities. The solvent crystallization method is similar to a lubricating oil dewaxing plant in operation, for instance, and it has been estimated that a winterizing unit similar to the ordinary large size dewaxing plant would be capable of turning out, at full capacity, the entire annual production of winterized salad oils in the United States in less than a week.

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Cane Sugar Refining

Centrifugals for Separation of Sugar Crystals from Liquor at Imperial Sugar Co., Sugar Land, Tex.

WILL H. SHEARON, JR.

Associate Editor

in collaboration with

W. H. LOUVIERE¹ AND R. M. LAPEROUSE

Imperial Sugar Co., Sugar Land, Tex.

THE average person today, knowing that sugar is an important diet staple all over the world (annual per capita consumption in this country is approximately 100 pounds) probably does not realize that sugar was not cultivated except in a limited portion of Asia until the fifth century A.D., and that there was no important traffic or refining in Europe until after the time of the Crusades. Taggart and Simon (23) have written a very readable history of sugar cane, its growth, and its processing. Table I condenses United States sugar production statistics for the past 25 years.

The discovery of the New World brought about a great change in the history of sugar, since the cane was introduced into the tropical areas by Columbus and Cortez, and by the seventeenth century the sugar industry in the tropical Americas was the greatest in the world. The Jesuit Fathers are credited with introduction of sugar cane into Louisiana in 1751, and, after almost a century passed, the first sugar cane was planted in Texas in 1840, on the Williams plantation, which was situated on the main road from Galveston to the West. The settlement which grew around this plantation was called, as it is today, Sugar Land. It is the site of the only sugar refining operations in the state of Texas and, incidentally, the only standard bone char sugar refinery between the Mississippi River and the Rocky Mountains.

Domestic raising of sugar cane in those early days was a profitable business, and the first sugar mill was erected on the planta-

tion in 1843, at approximately the spot where the refinery of the Imperial Sugar Co. now stands. So began a thriving industry in growing cane and milling sugar which continued, although reduced in size after the War between the States, up to the early 1900's. Increase in labor costs, tariff changes, plant diseases, and foreign competition gradually took their toll, however, and the last cane grown in Texas was processed at the old cane mill in Sugar Land in 1928.

Refining equipment had been added to the Sugar Land mill about 1890, and such a demand arose for the product of this refinery that importation of raw sugar was begun; the first cargo of Cuban raw cane sugar was brought through the port of Galveston in 1902. At this time the refinery capacity was less than 100,000 pounds per day.

The Cunningham Sugar Co. at Sugar Land, Tex., was in receivership around 1900, and W. T. Eldridge, who owned a small sugar mill nearby, bought the Cunningham sugar mill and properties. In 1905 the Kempner interests of Galveston formed a partnership with Eldridge and reorganized the sugar company, adding new machinery and methods of operation. The Kempner interests bought out the Eldridge interests in 1946 and under this ownership with I. H. Kempner, Sr., chairman of the board, the production capacity of the refinery has reached 2,000,000 pounds of refined cane sugar per day.

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² Technical Director, Imperial Sugar Co., Sugar Land, Tex.

TRADE GLOSSARY

Affination = process of washing sugar crystals with water to remove film of impurities adhering to crystals

Affination sirup = sirup spun off raw sugar crystals by centrifuging in the affination process and containing most of the impurities; green sirup is that centrifuged from first affination of raw sugar; wash sirup is that centrifuged off after the water wash step

Blackstrap = a dark and viscous liquid, separated from low grade massecuite, from which no further sugar can be obtained by usual methods; contains about 35% sucrose, 20% glucose or invert sugar, 10% ash, 20% moisture, and 15% organic non-sugars

Blowup tanks = tanks in which washed raw sugar liquor is raised in temperature before entering pressure filters

Boiling = concentration of liquor or sirups after initial evaporation; carried out in separate vacuum pans along with most of crystallization step

Brix degree = an arbitrary scale for conversion of saccharimeter reading of sugar solution into its specific gravity

Defecation = precipitation and coagulation of nonsugars from raw juice or raw sugar liquor by addition of chemicals such as lime and phosphoric acid

First liquor = clear, raw sugar liquor from first charcoal filter treatment

Footing = drawing grain from one pan into another pan containing grain and making a strike from that mixture

Graining = crystallizing sucrose from concentrated liquor or sirup by boiling under vacuum

Liquor = sugar solution that has never been concentrated to crystalline state (or from which crystallization has never taken place)

Low and high molasses = see Figure 9.

Magma = a pasty mixture of sugar and water similar to a massecuite but not obtained by evaporation

Massecuite = concentrated sirup consisting of crystalline sucrose surrounded by mother liquor, molasses

Purity = percentage of sugar as indicated by direct polarization with reference to total solids content as indicated by hydrometer density scale ($^{\circ}$ Brix)

Remelt = a sugar to be reprocessed

Return liquor = off-color filtrate obtained at end of washed sugar liquor cycle

Second liquor = also called filtered seconds; clear liquor from three-pass char filtration of affination sirup

Sirup = liquor from which sucrose has been crystallized

Soft sugar = small, spongy grains, high in invert sugar content, and ranging in color from almost white to a dark brown

Spinning = process of centrifuging a massecuite to remove excess sirup

Strike = a full pan of sugar crystals

Striking a pan = emptying a strike into a mixer prior to spinning

Sweetwater = washings from char before it goes to kilns for re-vivification

IMPERIAL SUGAR CO. OPERATIONS

Imperial gets its raw cane sugar from Cuba, Puerto Rico, and Louisiana, the latter supplying only about 10% of the plant's needs. It is shipped from the source in 325-pound bags and unloaded direct into railroad cars at Galveston or Texas City for the 60-mile trip to the refinery. Samples are taken at the point of unloading for the laboratory polariscope analyses on which the purchase price is based.

Although the production of raw sugar from cane will not be treated in detail in this article, it is well to consider briefly the major operations in obtaining it from cane, most of which are simplified versions of steps in the later refining process.

The cane is cut by hand or machine and brought to the mill where it is slashed into small pieces in a mechanical cutter and shredded. It is then passed through several sets of rolls, at a pressure of 300 to 600 tons, which squeeze the juice from the cane. Louisiana mills pioneered in the use of turbine drive for the mills rather than reciprocating steam engines and the employment of hydraulic accumulators to maintain pressure on the mill rolls (7).

Ventre (27) goes back to the early days and points out that the background of present-day farm-made sugar cane sirup was the discovery that extracted juices could be preserved by concentrating them into sirups by open boiling and that at the same time the coagulated and precipitated nonsugars could be removed by skimming. This same process is followed on a large scale—the raw juice is strained, clarified by addition of lime to remove impurities, heated, and then allowed to stand so that impurities will settle out.

From the settling tanks the clear juice is passed through multiple-effect evaporators where it is concentrated (the first triple-effect evaporator in the sugar industry is said to have been installed in 1834 by Rillieux on a Louisiana sugar plantation) and then into vacuum pans where sucrose or sugar is crystallized out. The mixture of crystallized sugar and sirup is centrifuged, and the raw sugar from the centrifuges is packed into 325-pound bags for shipment to refining plants. The crystals are brown in color and vary in size, usually being from 0.4 to 0.8 mm. in diameter. Basically, sugar refining consists in:

and char-filtered for removal of impurities and color, respectively

Recrystallizing and separating crystals from mother liquor
Washing with water and drying with heated air
Screening and packing

Receiving and Melting

The raw cane sugar, as received at the Imperial refinery, is discharged from the cars into a lump-breaking mechanism which consists of two shafts rotating toward each other, each mounted with 6- to 8-inch intermeshing fingers. Belt and bucket conveyers move the sugar to a slant-bottomed bin of 50-bag capacity. As may be seen from its small capacity, this bin is not considered as a storage bin, but it takes care of fluctuations in operation in the same manner that a surge tank operates with liquid flow.

The raw sugar drops by gravity out of the bin and is moved by conveyer to a shredder consisting of two shafts mounted with blades and revolving in opposite directions (Figure 1). From the shredder it drops into a mingler, 14 feet long and 3 feet wide, containing a 24-inch spiral conveyer element. This is a cut-flight element, as contrasted with other conveyers in the plant which are the helical ribbon or scroll-type conveyers. Since the raw sugar consists of nearly pure sucrose coated with a film of molasses it is desirable to soften the film for easy removal with a minimum of washing. Therefore affination sirup is added to the mingler from a 3000-gallon supply tank. The significance of this step lies in the fact that the raw sugar crystals are mixed with a sirup which is already saturated with respect to sucrose. Thus the residual molasses film, which contains most of the impurities, is washed off, and little of the crystalline sucrose goes into solution.

TABLE I. UNITED STATES SUGAR SUPPLY AND CONSUMPTION^a

Year	Production, Thous. Short Tons		Consumption		Exports, Thous Short Tons
	Domestic	Refined from imported raws	Total, thous. short tons	Per capita	
1925	2875	3296	6171	107.5	379.4
1930	3490	2781	6271	99.4	77.8
1935	4142	1838	6246	97.1	114.0
1940	4610	1788	6398	97.2	169.9
1945	2842	2855	5696	81.2	290.6
1949	3527	3443	6970	92.6	43.7

^a Data from Sugar Reference Book, Vol. XIX, 1951.

Washing the raw sugar crystals free of most impurities
Melting the washed sugar into a sirup which is then press-

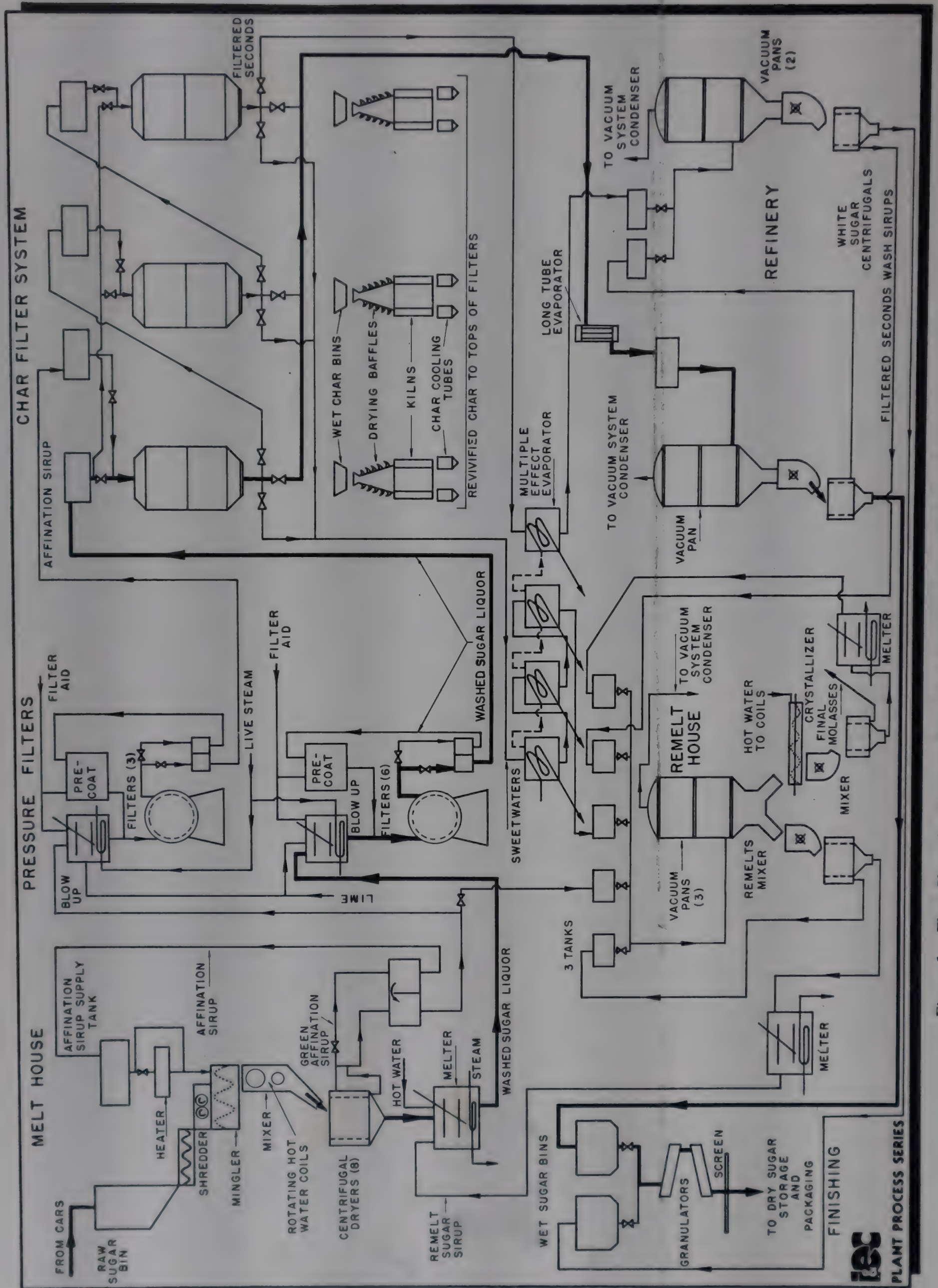


Figure 1. Flow Sheet for Refining Raw Cane Sugar at Imperial Sugar Co., Sugar Land, Tex.

Thirty-five pounds of affination sirup (80° Brix) are added per 65 pounds of raw sugar (99° Brix) to obtain a magma of 94° Brix. The addition is controlled by a hand valve in accordance with ammeter readings. These readings are a direct indication of the pull on the mingler motor and are used as a measure of the density of the mixture.

The massecuite then drops between two oppositely revolving rolls 0.5-inch apart and into the raw sugar mixer. This mixer is equipped with rotating hot water coils (16E), and automatic temperature controls and will handle approximately 90,000 pounds per hour. The massecuite is brought to 150° F. and kept constantly in motion until the centrifugal separators just below the mixer are ready to receive it.

Invention of the centrifugal machine used in the sugar industry has been credited to Hardman (27) in 1843 and Penzoldt (17) in 1837, and the suspended centrifugal of the type now used to Weston (21) in 1852. Regardless, its invention revolutionized the sugar industry, which up to that time had settled concentrated massecuite in hogsheads and drained off the molasses through small holes in the hogshead bottom.

At Sugar Land there are eight of these centrifugals (16E), which have perforated baskets (40 inches diameter by 24 inches deep) backed by perforated screens with 400 holes (0.027 inch diameter) per square inch. The baskets revolve at 1500 r.p.m.; each group of four machines is powered by a 250-hp. motor. The liquor, termed green affination sirup, is expelled through the sides of the basket and flows from the centrifugal through a trough to a two-compartment supply tank. The sugar is then subjected to a spray of wash water (130° F.) while the centrifuge is still moving (wash affination sirup results); the machine is braked, and the sugar is scraped off the sides of the basket by plows and dropped through a port in the bottom of the basket. All operations in the cycle are automatically controlled with the exception of the filling and plowing off of the sugar, which are controlled by gate valve and handwheel, respectively. The entire centrifuging and washing cycle, steps of which are shown in Table II, consumes approximately 2.5 minutes and 2 to 3 gallons of water per cycle. The washed sugar is moved by conveyer to a 2000-gallon melting tank equipped with paddle-type agitators and steam coils; here hot water is added to produce a liquor of approximately 59.5° Brix, at 160° F. It is then pumped over screens to the blowup tanks at the press filter station.

The wash affination sirup from the centrifuges passes into the affination sirup pump tank and from there is pumped to the supply tank to be used for mingling with the raw sugar. Excess wash affination sirup spills over into the "green" compartment of the pump tank and the mixture is either pumped directly to the



Figure 2. Washing Down a Pressure Filter

remelt house or is defecated and press-filtered and pumped to the char house.

Some sugar remains on the burlap bags in which the raw sugar is shipped, and economy demands its recovery since nearly 7000 bags per day are received. If the bags are substantially dry when emptied at Sugar Land, they are tumbled in a large rotating drum with an air blast to aid in removing adhering sugar, and the recovered sugar is fed into the main process stream. If received wet, the sugar is washed out and the bags are dried on the kiln floor in the char house. Some refineries make no distinction between wet and dry bags and wash both. During World War II cleaned bags were returned to the raw sugar mills; today and generally, however, they are sold to bag manufacturers and are commonly used in baling cotton.

Defecation and Filtration

Before describing the highly important but relatively simple and clear-cut press filter operations, as practiced at Sugar Land, the reasons for this step and some of the history of the techniques adopted by the sugar industry as a whole may be of interest.

Ventre (27) says that when the early raw sugar mills began adding lime before boiling to aid in precipitation and coagulation of nonsugars and discovered that these sirups when highly concentrated gave a larger quantity of crystals than those not treated, the use of lime as a defecant or clarifier was firmly established. Raw sugar tends to be somewhat on the acid side, and the most important action of the lime is to raise the pH of the washed sugar liquor to slightly beyond neutral and prevent inversion of the sucrose. Phosphoric acid (0.025 to 0.05% of the solids in the melt) may also be added with the lime, and the flocculent precipitate of calcium phosphate which is thus produced acts as a clarifying agent in absorbing and enmeshing the suspended and colloidal matter and removing some of the color.

Actually, the use of phosphoric acid has fluctuated; it was the standard defecant in America when the bag filter was in vogue but was more or less discarded when leaf pressure presses first displaced bag filters about 1913. The characteristic of most value in removing impurities—flocculence of the precipitate—offered considerable difficulties in the leaf filters because of slow filtration rates and inversion losses. Diatomaceous earth (Table IV) is added to aid the filtration of the flocculent precipitate, but Cummins (2) points out that lime, phosphate, and the usual filter aid together have not proved entirely satisfactory as the calcium phosphate floc clogged the pores in the diatomaceous filter cake. Because of this, filter aid and lime only were used for some time, but recently developed, fast flow filter aids will give good filtration even when phosphates are used, with advantages of better clarification and removal of some color (not obtained with the old slow rate aids and without phosphoric acid). Imperial's produc-

TABLE II. TIME CYCLE FOR RAW SUGAR CENTRIFUGAL STATION

Operation	Time, Seconds
Spin	25.0
Wash	4.0
Spin	20.0
Wash	8.5
Spin	27.5
Brake	40.0
Plow	25.0
	150.0 (2.5 minutes)

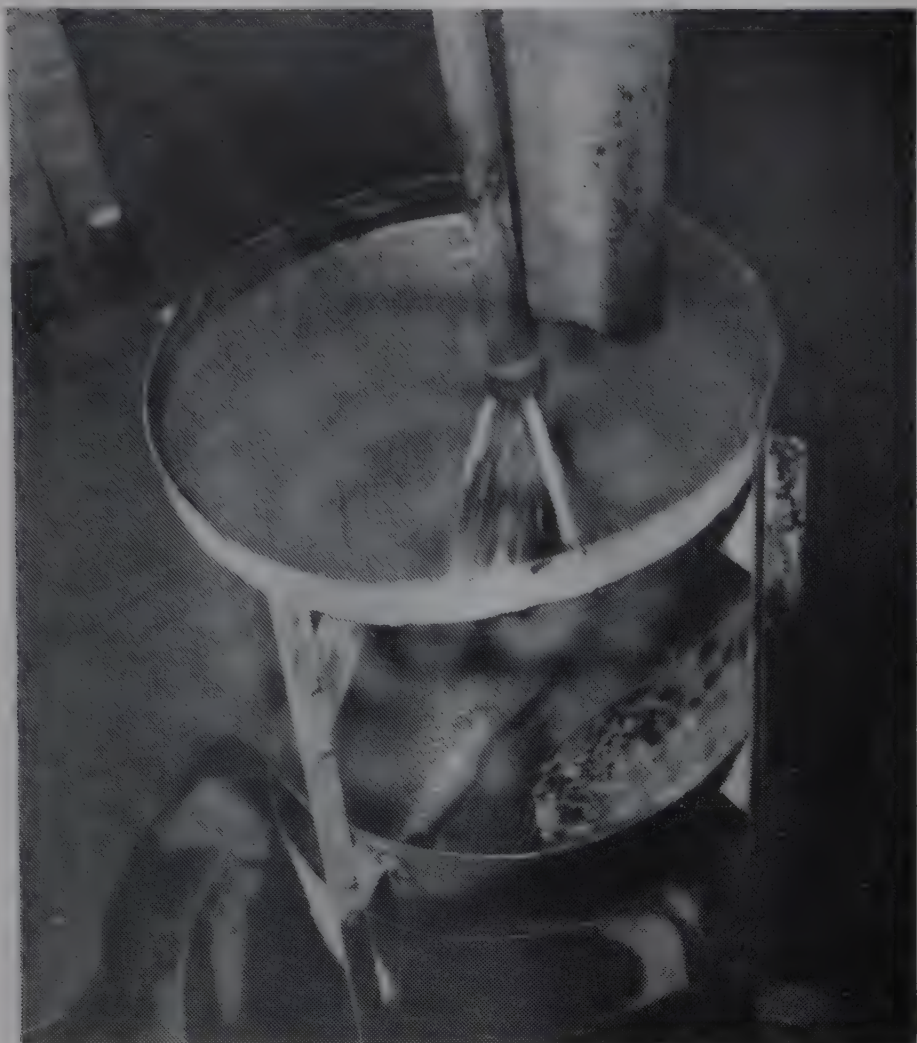


Figure 3. Staggered Funnel for Premixing Char and Liquors

tion executives, however, question whether the cost of the additional quantities of filter aid required in this technique are justified by the results obtained.

Vallez rotary leaf filters were first used in the sugar industry in the early 1920's, and Knowles (16) recommends the use of these filters, with paper pulp medium and at low pressure, for filtering calcium phosphate floc. The Wright cord filter (31) has been suggested in continuous filtration where a combination of defecant and filter aid has been used. Of more than 750 materials which have been suggested as defecants, only lime, phosphoric acid, diatomaceous earth, and sulfur dioxide (mainly in the beet sugar industry) are generally used in clarification of raw sugar juices and liquors. More than 90% of the domestic cane sugars today are made from raw sugars clarified by heat and lime. The British claim to produce a sugar of better quality by use of an additional technique (17) which they term "carbonatation"; this involves bubbling carbon dioxide through the liquor being defecated. The method has not been used in America owing to the available supply of domestic filter aids. It is understood at the present time, however, that a refinery in this country is planning an installation of this type.

Defecation as practiced at Sugar Land involves treating both the washed sugar liquor and the wash affination sirup in paddle-agitated blowup tanks, each 1000-gallon operating capacity. The tanks are heated to 190° F. by means of coiled open steam pipe, which also provides some agitation. Calcium hydroxide, in the form of a 15° Brix water suspension is added to the blowup tanks by hand in the quantity necessary to raise the pH to about 7.3, and diatomaceous earth is introduced through a chute. Operators check the pH at the presses using colorimetric methods, and results are confirmed by the laboratory. Orthophosphoric acid is occasionally added to affination sirup as determined by the color of the affination sirup and by the extent to which the char filters are providing decoloration.

The defecated liquor is passed through presses (8E) which have been precoated with filter aid and emerges from the presses ready for decolorizing by the char. Six presses are available for washed sugar liquor and three for wash affination sirup.

These have 72 leaves each, 37 inches in diameter, and 1044 square feet of filter area. Individual presses are operated from 3 to 12 hours (depending on the quality of the liquor or sirup being filtered) before it is necessary to sluice down with water (Figure 2) and drop the cake. Maximum sucrose lost in the press cake never exceeds 0.5% of the filter aid discarded, and more frequently, as is shown by laboratory analysis, is almost zero.

Decolorizing

The sugar liquor as it comes from the presses, amber in color, must be decolorized before it is concentrated for the crystallization step. It is therefore passed through bone char filters in what is known as the char house. At Sugar Land this unit of the plant consists of 3 houses, each containing ten filters, all operated under a pressure of 15 pounds per square inch gage. These vessels, vertical iron cylinders 10 feet in diameter by 21 feet high, have an operating capacity of 1250 cubic feet each of bone char (largely calcium phosphate, with about 10% carbon), which is fed in at the top and rests on a perforated bottom in the base of the filters; approximately 70% of new char is retained on a 16-mesh screen, whereas with the poorest grade approximately 70% is retained on a 35-mesh screen. In filling the filters a small amount of dry bone char is added first, then liquor and char are introduced together via a staggered funnel (Figure 3). This concurrent introduction is carried out to reduce attrition, to minimize channeling, and to dissipate the heat formed as a result of the heat of wetting of the char. There is still disagreement in the industry, however, regarding the relative advantages and disadvantages of wet and dry filling.

Washed sugar liquor from the filter presses is pumped into one of four 4300-gallon supply tanks, from which it is fed by gravity into the top of the filters in one of the houses and emerges from the bottom of the filters as a clear liquid (near water-white), designated as first liquor and ready for the refinery. This product is 99.7 apparent purity, with a solids content of 64° Brix.

Affination sirup is given a different and much more extensive treatment. After defecation and press filtration it is pumped to one of the supply tanks, from which it flows by gravity into the first or A house, where it percolates through the charcoal in a manner similar to the raw sugar liquor. From this set of filters, however, it is pumped to a second supply tank and thence into the B house filters, where it is given a similar filtration. After this second treatment it is again transferred to a supply tank and into the C house filters, from which it finally emerges as second liquor, or filtered seconds.



Figure 4. Emptying a Char Filter to Revivification Unit

Table III shows a typical 80-hour cycle for the char filters. The end of the washed sugar liquor cycle is denoted by the appearance of an off-color filtrate or return liquor, and this cycle is followed by the affination sirup cycle. Even after the affination sirup has been introduced into the filters the return liquor is still run off the filters until the apparent purity reaches 97.5; at this time the percolate is directed to the supply tank for further decolorization.

TABLE III. TYPICAL OPERATING SCHEDULE FOR CHAR FILTERS

Operation	Material	Time, Hours
Fill cell	Revivified carbon and light color sirup	8
Filter	Return liquor	8
Filter	Washed sugar liquor, principal product flow	16
Filter	Affination sirup as follows:	8
	A house, sirup from melter	
	B house, filtered sirup from A	
	C house, filtered sirup from B	
Wash char	Water, removing sirups to produce heavy sweetwater	10
Wash char	Water, removing sirups to produce light sweetwater	5
Wash char	Hot water, removing soluble impurities	18
Blow	Air, removing water from the char	5
Empty	Exhausted char to revivifying kilns	2
	Total	80

Control of the liquors and sirups to and from the various filters during the steps in the 80-hour cycle is accomplished from what is known as the liquor gallery. This consists of a series of long rectangular metal troughs each of which is designated to receive a particular material. Mounted on top of and at right angles to these troughs is a series of short troughs which may be moved back and forth so that their outlets discharge into any long trough desired. Above each of these short troughs is the discharge spigot of a flow line.

Char Revivification. After 32 hours of decolorizing, the char is usually exhausted and must be revivified. A 10-hour period of washing with water at a rate of 500 gallons per hour produces a heavy sweetwater, and a light sweetwater results from an additional 5-hour washing. The combined sweetwaters are concentrated by use of exhaust steam in the first three bodies of a falling film evaporator and are pumped to the remelt house.

The carbon is further washed with 2500 to 3000 gallons of water per hour, for approximately 18 hours, to remove soluble impurities and is emptied from the bottom of the filters (Figure 4) into wet char bins above the revivifying units. Moisture content of the char at this point is approximately 18%.

The revivifying units consist of gas-fired kilns each having two sets of retorts on each side of the firebox. The char passes first along a set of drying baffles mounted on the exterior surface of the flue gas exit from the retorts, and moisture is removed by convection evaporation. It then drops into the top of closed retorts, and thus at no time comes into actual contact with the flue gases. Two types of retorts are used, cast iron and chrome steel. The former are oval shaped, 3 by 12 inches in diameter and 8 feet 4.5 inches long. These are set in four rows of twenty retorts each per kiln unit, or eighty retorts. The chrome steel retorts are round (3.25 inches in diameter by 8 feet high) 28-gage 17% chromium oil burner steel tubes (11E), and in order to equal the capacity of the cast-iron retorts, 240 are required per kiln unit.

Retorts are operated on a straight-through basis, with the char heated to approximately 1000° F. About 5 hours—half of this time in the kilns—are required for char to travel through the entire revivification system. The operators check the quality of the revivified char by heating it with caustic soda solution. This is a visual test, and a very light amber color after heating indicates proper revivification. The revivified char, from which impurities have been burned, is automatically proportioned into vertical char cooling tubes and onto a belt conveyer (Figure 5). By the time the char reaches the conveyer it has cooled to approximately 230° F. and in the conveying equipment is further reduced in temperature to 180° F. before reaching the top of the filters.



Figure 5. Revivified Char from Bottom of Retorts Is Belt-Conveyed to Filters

Magnet separates traces of metal

Fines are removed continuously, by passing the char over 50-mesh vibrating screens; new char is introduced into the best grade char, and poorer grades are systematically moved over to the other houses. Wash sugar liquor may be decolorized over new char or any grade of used char immediately after the char has been revivified. Affination sirup, however, is filtered progressively from the A house to the C house, through the poorest to the best grade of char.

As far as the rest of the industry is concerned, most of this country's large refineries use bone char filtration systems. Some plants, notably small refiners who cannot afford the initial building and equipment investment and the tremendous inventory of bone char which must be kept on hand use vegetable carbon. This type char is strictly an activated carbon as contrasted to bone char, which is not considered activated in the true sense. Vegetable chars have greater decolorizing efficiency (smaller quantities are required) and are less expensive than bone char in actual cost per pound. The bone char process, using large masses of char, removes more ash than is possible with the relatively small quantities of vegetable char used in that method. Vegetable chars are heated directly with the liquors and filtered out and discarded after each cycle. Among the activated carbons, Hertzog and Broderick (10) have described the preparation of such materials even from coal and coal refuse.

Evaporation and Crystallization

Although all the previous steps are considered portions of the process of refining raw sugar, it is the equipment for evaporation, boiling, and crystallization that constitutes the part of the plant actually called the refinery. Van Hook (26) points out that these three operations are distinct and separate steps in sugar refining, although in fact the boiling and crystallizing steps are carried out in the same equipment and are the only steps in the entire process that are not essentially continuous.



Figure 6. New Low Head Vacuum Pan, Control, and Sampling Area

Sucrose does not crystallize when a saturated solution is reached but the solutions attain a degree of supersaturation depending on the temperature, and crystallization is usually started by seeding. The first liquor, as it comes from Imperial's char filter, is at 64° Brix and 99.7 apparent purity, and contains about 55 pounds of water for each 100 pounds of sucrose. In order to reach simply the saturation point at the range of temperature in the white sugar vacuum pans, it is therefore necessary to evaporate 25 pounds of water per 100 pounds of sucrose. With thin liquors such as filtered seconds, the amount of water which must be evaporated is significantly greater.

Removal of this water in various steps instead of one single evaporation has evolved over a period of years in the sugar industry as the most economical method. All the steps, however, have the common purpose of reducing the water to sugar ratio to the point necessary for crystallization and doing so in the least possible time at the lowest temperature practicable in order to reduce caramelization and inversion. Since a considerable portion of the water can be evaporated before close control becomes necessary, this can be carried out in a standard type evaporator.

The general tendency in the industry today is toward the calandria type—a vertical evaporator in which the liquor is in the tubes which are heated by steam on the outside—and the effect is similar to that of a coffee percolator. Imperial has installed the long tube modification (4E) of this evaporator for pre-evaporation of first liquor. This evaporator has a 7 × 7 foot vapor head mounted directly over the long tube (18 feet) heating element. The juice makes a single pass at high velocity through the tubes, resulting in very rapid heat transfer.

Pre-evaporation of first liquor was carried out for a long time

at Sugar Land in the fourth body of a quadruple effect, falling-film evaporator (10E), a type still common in the sugar industry; filtered seconds were concentrated in the third body and sweetwaters in the first two. Since installation of the long tube evaporator, the fourth body of the falling-film evaporator is used for filtered seconds, and the remaining three bodies are reserved for sweetwaters.

The falling-film evaporator consists of a horizontal cylindrical body filled with tubes vented at one end and fitted into a tube sheet at the other. Steam is admitted into the tubes, and the liquor to be evaporated is sprayed in a continuous film over the tubes; concentrated liquor leaves the evaporator at the bottom. The tubes are slightly inclined to allow condensed steam to flow back into the steam chest and leave through a discharge pipe. In the evaporator in use at Sugar Land each body has 331 tubes, 3 inches in diameter and 7 feet long, holds 322 gallons of liquor, and is capable of handling 12,000 gallons of liquor per hour. Tube heating area is 1818.7 square feet, and the tube sheet area is 297.04 square feet.

During pre-evaporation the density of the liquor is increased from 64° to 70° Brix, and the concentrated liquor is pumped to a central supply tank before it enters the boiling stage. It is in this stage that very careful attention is first required since this is the point of maximum concentration and minimum bulk and the most critical part of the process in so far as proper crystallization and prevention of formation of degradation products are concerned.

The steam heated vacuum pan invented by Howard in 1813 was quickly adopted by sugar refineries to prevent losses due to inversion and caramelization caused in open direct-fired kettles. For many years, however, sugar boiling and crystallization remained entirely an art, and it was not until recently (25) that instrumental regulation of vacuum pans became a reality. Many sugar refinery operators have yet to be convinced that boiling by instrument alone will produce a satisfactory sugar, although they admit that instrumentation as an adjunct to the judgment of a trained boiler is valuable. Webre (29), in discussing the design and use of pan control instruments, assigns the highest importance to control for producing a constant and uniform vacuum. Without this, he says, control instruments of any kind are unreliable, and with it, the necessity for them is much reduced.

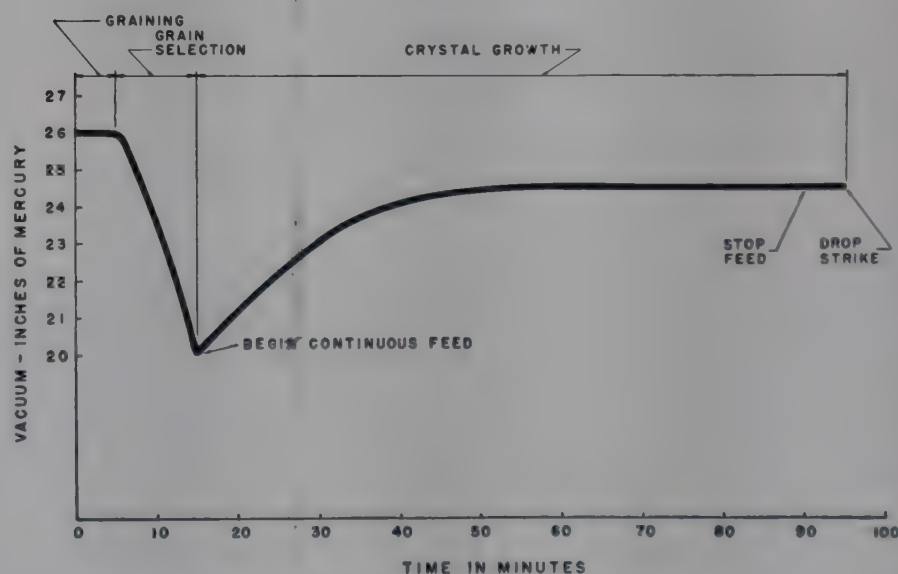


Figure 7. Typical White Sugar Crystallization Curve

The vacuum pan is essentially a vertical single-stage evaporator heated by live steam and may be of the coil or the calandria type. All of Imperial's pans until recently were of the coil type, in which steam is carried by independent copper tubes in the form of a conical spiral; the tubes are placed at intervals up to about two thirds the height of the pan. In general, all equipment used for handling first liquors is copper; wrought and cast iron are sometimes used, but copper and stainless steel vessels and piping are most desirable. In the new addition to its plant, however, Imperial has kept pace with the trend toward use of the calandria-

type pan, and all new pans installed are of this type. These low head vacuum pans (12E) carry the concentrated liquor or sirups in vertical tubes (4 inches outside diameter and 4.25 feet high) set in a tube sheet in the steam space (10 feet diameter) at the bottom of the pan (Figure 6). Above the tube sheet there is a 12-foot diameter circulating and vapor disengagement area, to which the vacuum system is connected, and a 4-foot diameter downtake which extends through the calandria section only. There are a number of advantages and disadvantages for both types of pans (5, 21), but dish-bottomed improvements in the calandria pan and the less rigid attention to maintenance demanded by this latter type are contributing to its popularity.

White Sugar Crystallization. A small quantity of concentrated first liquor is introduced into the 14-foot diameter pan designated as No. 4 (1700 cubic feet capacity) where it is heated to 180–165° under a vacuum of 20 to 24 inches, respectively. The initial evaporation step in this crystallization operation is actually started with approximately 26 inches vacuum and proceeds, as is shown in Figure 7, until as additional water is removed a supersaturation of approximately 1.37 is reached. In the fundamental considerations of sugar crystallization this is the transition zone.

There are three zones of supersaturation:

The metastable, where there is a tendency for crystals to grow but not for new crystals to form

The transition, where new crystals will form but only if nuclei are present

The labile, where free crystallization occurs

When the sugar boiler has brought the liquor to the transition zone, he seeds or shocks the supersaturated liquor and holds it there for a period of graining, until the desired number of nuclei are formed, then returns it to the metastable zone, where the nuclei will grow but no new ones will form. If he should go beyond the metastable to the labile zone, crystals of improper size or shape, called false grain, are likely to appear.

Sugar Land boilers use pulverized sugar as seed crystals. The vacuum under which the pan is operating sucks pulverized sugar from a container into the pan through a tube attached to the pan and regulated by a valve. At the end of the graining period the boiler returns the massecuite to the metastable stage by reducing the degree of supersaturation. Vacuum is reduced rather abruptly from 26 to 19 or 20 inches, and during this time, which might be termed a grain selection period, soft and poorly formed crystals dissolve, leaving only hard and better crystals. These crystals belong to the monoclinic system, and well formed ones are generally dodecahedral or twelve-faced. The boiler must be careful not to operate below the minimum vacuum, or supersaturation will be reduced to such an extent that all the crystals will be redissolved.

When the boiler is certain that proper crystal growth will occur in the massecuite, he starts feeding liquor into the pan and gradually raises the vacuum until it is up to 24 inches. He then continues to boil the sirup until the proper solids content (90° Brix) is reached; the feed is cut off about 5 minutes before the sugar is struck to the mixer. Approximately 95 minutes are required to make a strike from first liquor, and when the pan is emptied to the mixers about 80,000 pounds of dry granulated sugar are obtained. One paddle-agitated mixer (2054 cubic feet capacity) serves the eight belt-driven centrifugals (16E) which are similar in operation to those already described in the melt-house. This mixer serves as a surge tank and aids in maintaining the fluidity of the massecuite; it is highly desirable that the massecuite be dropped to the centrifugals as quickly as possible with the minimum or no changes in its physical characteristics.

Sugar from the centrifuges is conveyed to the No. 1 wet sugar bin and the first sirup, 98.5 apparent purity, is pumped to a 4000-gallon supply tank for further working. Figure 8 shows the steps through which this sirup is carried in order to produce an additional 80,000 pounds of white sugar. All sirups are concentrated either

in No. 1 pan (capacity 772 cubic feet) or No. 2 (capacity 1000 cubic feet). Two strikes of first liquor from the No. 4 pan are necessary to produce sufficient first sirup to make a strike from the No. 1 or 2 pans, and this generally applies to the sirup steps also. All sugars from these additional strikes are conveyed to the No. 2 wet sugar bin. Five belt-driven centrifugals and a 949-cubic foot mixer serve these pans. On the average a larger number of white sugar boilings can be made in factories that use bone char in the decolorizing step than in those that employ vegetable char (26).

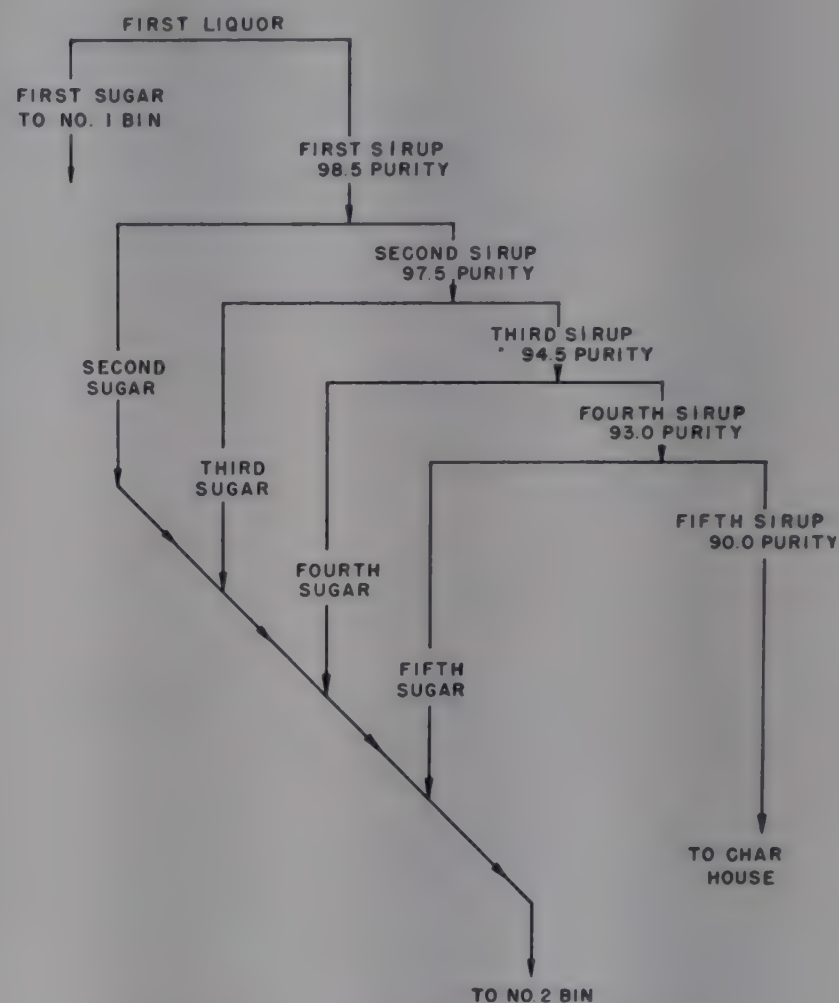


Figure 8. Stepwise Sugar Crystallization

In the white sugar house there is another and smaller (327-cubic foot) vacuum pan used entirely for processing filtered seconds. This pan is served by one centrifugal machine and a 393-cubic foot mixer. The liquor (filtered seconds) from three passes through the char filters goes to the fourth body of the falling-film evaporator, entering at 58° Brix, and is concentrated to 68°. From this pre-evaporation it is pumped to a 4000-gallon supply tank from which it is pulled by vacuum to the No. 3 pan; sugar strikes from this pan go to the No. 2 wet sugar bin, and the filtered seconds wash sirups are transferred to the remelt house.

As this article goes to press a part of the white sugar equipment at Sugar Land (No. 1, 2, and 3 pans) is being shut down, and white sugar operations other than first liquor processing are being transferred temporarily to a new building designed to eventually operate as the remelt house. The old white sugar installation will be replaced with calandria-type equipment (already described in the preceding section) and centrifugals of an advanced design. Two 1000-cubic foot pans, with 10-foot calandria section and 12-foot vapor space, will take the place of the three smaller pans now in use, and a 2000-foot pan will be substituted for the 1700-foot pan used for processing first liquor. The 4000-gallon tanks used for supply in the old white sugar house will be replaced with 10,000-gallon tanks such as have been installed in the new addition. These were designed and fabricated locally (17E) and are dish-bottomed circular tanks, 12 × 12 feet.

Two of the new calandria-type 1000-cubic foot pans have already been installed in the new addition and are being used in place of white sugar pans Nos. 1, 2, and 3 for processing first liquor sirups and/or filtered seconds. A third is ready for installation as dismantling of the old white sugar house progresses.

(sugar crystals retained on 8 mesh) from the lower granulator are melted and returned to the process, and the dry sugar goes to stainless steel-clad storage bins with 2,000,000-pound capacity.

Dry sugar from the storage bins is screened through Rotex screens and packed by automatic machinery in 2-, 5-, and 10-pound packages (3E) and 100-pound bulk bags (14E). The packaging room at Sugar Land is the only air-conditioned installation in the sugar industry.

LABORATORY

Laboratory control is around the clock; routine analyses are made on sugars, liquors, sirups, and massecuites at each step in the process, and on the filter cake and waste waters. Liquors and wash waters from the char filters are tested frequently and changes that must be made in flow from the filters are determined by these. Chars are tested as they come from the kilns in order to maintain proper revivification, and a complete analysis of the char is made monthly to detect deterioration.

Most important function of the routine laboratory is to advise the sugar boilers of the condition of their liquors and sirups, particularly as regards purity and color. Hence the important routine tests are determination of Brix, purity, pH, and color. This laboratory also advises the operators when to ditch sweet-water and dump press cake.

The sugar balance, all important in any sugar refinery, is handled by the research laboratory. Complete analyses (sucrose, invert sugar, ash, moisture, organic nonsugars) are made on all raw sugars entering and finished sugars leaving the refinery. Costs are watched closely in the sugar industry as it operates on very small margins of profit. Average yearly prices in this country for the last 25 years show the small spread between raw and refined sugar prices:

Year	Wholesale Prices, Cents per Pound ^a	
	Raw	Refined
1925	4.334	5.483
1930	3.387	4.634
1935	3.220	4.316
1940	2.790	3.809 ^b
1945	3.750	4.855 ^b

^a Data from Sugar Reference Book and Directory, Vol. XVI, 1948.

^b Does not include processing tax of 0.535 cent/lb.

Raw sugar analyses are made by the seller, the buyer, and a referee, and Imperial's research laboratory makes the very careful buyer's tests. These tests are made with a polariscope and are based on the rotation in angular degrees which a calculated 100% solution of pure sucrose 100 mm. in length would give to a plane of polarized light. Using 26 grams of pure sucrose in 100 ml. of water to obtain an empirical reading of 100° polarization on the instrument, intermediate values in degrees read directly the percentage of pure sucrose in any solution. Sugar is generally sold on the basis of 96° polarization, with a bonus above that figure and a penalty below, as follows:

94°	-2.0%
95°	-1.6%
96°	...
97°	+1.5%
98°	+1.25%

There is no additional bonus for polarization values above 98°, and raw sugar producers generally attempt to stick to the 96° material.

Other tests such as color values on brown sugars are made by the research laboratory. Many companies use an empirical method in which the sugars are compared with standards made of ground, colored glass. Imperial, however, uses an instrument (1E) employing the reflectance method discussed by Gillett and Holven (6).

Finally, numerous special problems and occasional customer complaints are handled in the laboratory.

UTILITIES AND MATERIALS

Table IV indicates the average consumption of utilities and materials per ton of refined sugar produced.

The successful operation of a sugar refinery is dependent to a great extent on the quality of process water used. Distilled

water is the most desirable, but any water low in total solids, particularly sodium chloride, can be used. The importance of low dissolved solids content lies in the fact that their presence retards the crystallization of sucrose. As much as 3 parts of sucrose are prevented from crystallizing for every part of dissolved salts.

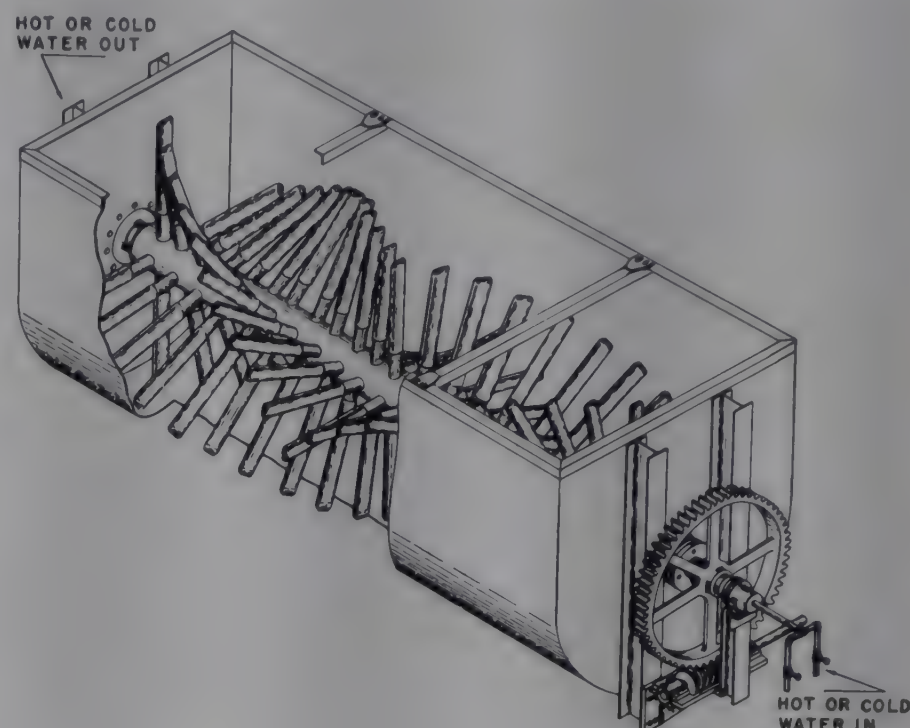


Figure 10. Crystallizer

Imperial's water is obtained entirely from deep well sources (750 feet), the strata affording minimum undesirable constituents, but treatment of this water is necessary before it can be used. The water treatment plant is a modern cold process installation (6E). A concentrated lime-water suspension is proportioned into the incoming raw water, and the treated water, together with 4 to 5 volumes of recirculated slurry, passes into secondary mixing and reaction zones where slow stirring and sludge contact bring the reactions to equilibrium. The water is then discharged into the outer portion of the treatment unit where the solids are allowed to settle. Clarified water is then sand filtered and pumped into cold water service lines or to an 80,000-gallon hot process water heater. In this unit, heated by exhaust steam supplemented by live steam to maintain a temperature slightly above 212° F. at 5 pounds per square inch pressure, further precipitation takes place. This water, following another sand filtration, is used principally for washing char in the bone char filters. Table V gives a typical analysis of process water before and after treatment and after heating.

TABLE IV. UTILITIES AND RAW MATERIALS CONSUMPTION
Consumed/Ton Refined Sugar

Water, gal.	600
Steam, lb.	3600
Natural gas, cu. ft.	4000
Electricity, kw.-hr.	44
Diatomaceous earth, lb	13
Bone char, lb.	2.75
Lime, lb.	1.0

TABLE V. TYPICAL PROCESS WATER ANALYSIS

	Raw Well Water, Grains/Gal.	Treated Water, Grains/Gal.	
		To heater	From heater
Dissolved solids	20.50	11.20	9.25
Hardness	11.75	3.40	1.75
Ghost point	9.80	1.75	1.25
Alkalinity			
Phenolphthalein		1.45	0.45
Methyl orange	10.50	2.25	0.90
Total chlorides	6.00	6.00	5.75



Imperial Sugar Co. Refinery, Sugar Land, Tex.

Natural gas, 1030 B.t.u. per cubic foot heat content, is used as fuel, and there is available a generator capacity of 3000 kv.-amp. at 2300 volts and 60 cycles. The steam plant, installed in 1938 (19), was the first open-air industrial structure of any significance in the Southwest.

FUTURE PROSPECTS

The sugar industry is progressive but most conservative in regard to process changes. Sugar refining is still an "art" and the industry operates on such a slender margin between profit and loss that new developments are regarded with a suspicious eye until careful evaluation has proved their worth beyond any doubt. As a result, not many innovations have been made industry-wide in the last 25 years. Imperial's refinery is considered one of the most modern in existence, and its expansion and modernization program confirms that. However, its bone char filtration system, for instance, although considered the "last word," is almost a quarter of a century old.

However, as pointed out by Rice (20), the entire bone char system used in the sugar industry needs overhauling, even though sugar production costs favor bone char over vegetable char for installations of any significant size. He proposed an improvement in revivifying char by using revolving iron drums and allowing hot products of combustion from fuel oil burned with controlled amounts of air to come in contact with the char and reactivate it. Rice's experiments were never carried entirely to completion on a large scale, however, and it is not believed that any commercial use has been made of them. Lyle (17) states very plainly that the bone char kiln is probably the most inefficient tool in sugar refining, and improvements are long overdue. Bone char research projects have been carried on for a number of years by a group of

sugar refiners with the cooperation of the National Bureau of Standards. Dietz (3) has completed a comprehensive bibliography of solid adsorbents. The multiple-hearth furnace (13E) has been installed in one American and one British plant and has given very satisfactory service. Rotating dryer-coolers (7E) have also been recommended for the revivification step. Because of the petroleum industry's tremendous success in fluidizing techniques, considerable study has been given to the adaptation of fluidizing to the revivifying of bone char. McLellan (18) has reported in detail concerning this. Some of its advantages appear to be low equipment cost, excellent heat transfer, cleanliness, particle sizing effect, and good heat economy. Possible disadvantages include need for multiple beds, excessive attrition rates, high power requirements, and necessity for fully automatic control. Work has also been done on a synthetic bone char (2E), and installations using this are planned by two companies. The drying operation in bone char revivification may perhaps be singled out as best suited for investigation in fluidized beds, since present dryers are not entirely adequate, but any estimates of the value of the fluidized bed technique for such use should be based on a comparison with the new equipment being developed by DeVries to be described at the Technical Session on Bone Char Research in Washington, D. C. in May 1951. Either the fluidized bed or the DeVries type dryer might be particularly well adapted for drying and heating the char after complete removal of adsorbed salts.

In refinery clarification the flotation technique of Williamson (30) and Jacobs (8, 15), which involves aerating and floating off calcium phosphate flocs (including various heating modifications), is attaining considerable use. No press filtration is required, and 30 to 40% decolorization of liquors is claimed. Ion exchange has been extended to sugar refining (1, 12, 14) but is much more satisfactorily adapted to refining beet sugar than cane. Principal reason for this is that the high acidity existing during most of the ion exchange step catalyzes the formation of noncrystallizable invert sugar. The first installation for deionizing cane sirup, however, is in operation at the Valentine Sugar Co. in Louisiana. A

few units have been installed utilizing the Sucro-Blanc process (15E), which uses chlorine as a defecating and bleaching agent and substitutes bauxite for the char as a decolorizer.

In the crystallization field much needs to be learned. Holven (11) discovered that, at all pressures encountered in the usual boiling of sugar, boiling points of sugar solutions of any degree of supersaturation plotted against the corresponding boiling points of water at these same absolute pressures yielded a straight line. This principle has been adapted to an automatic instrument for continuously recording and controlling the degree of supersaturation. The rate of crystallization is a primary factor in determining plant requirements and cost of operation. Van Hook (24) has studied in some detail the effects of impurities on the velocity of crystallization and has determined that the crystallization of sucrose from supersaturated solutions follows the monomolecular law. He holds that these rates are independent of diffusion rates or viscosity and are influenced by some kind of interfacial reaction, probably of a chemical rather than a physical nature. Proper seed or grain is absolutely necessary to produce final crystals of any specified size and distribution, and it has been pointed out (25) that, although little work has been done on the scientific aspects of this operation, its technical importance seems to be implied in various new systems of graining and boiling.

Industrial Uses and By-Products

The greatest industrial uses of sugar as such are in the food industries, but it is also an important raw material in nonfood fields, ranging from the preparation of hair tonics and shoe polishes to photographic materials and pharmaceuticals. Histadine and histamine are made with sugar as a raw material, and direct reaction of sugar with various chemicals can produce resins, denaturing agents, and plasticizers.

Among the many research projects completed or in progress under the guidance of the Sugar Research Foundation (22) are a number dealing with derivatives of processed sugar itself for possible industrial applications. Some of these are esters such as octafuroyl-, octaanisoyl-, tritosyl-, and pentaacetyltritosyl-sucrose. Ethylene oxide derivatives have been prepared for experimental study. Certain sugar derivatives which should be effective as surface active (wetting) agents are being studied. Another interesting project has been the development of pre-packaged smudge and heating units utilizing sugar as a fuel, and detailed directions for the use of sugar in manufacturing briquets for this purpose were worked out.

No discussion of the future of sugar would be complete without mentioning the products resulting from the processing of cane. Eads (4) has discussed recent developments in sugar by-product chemical research. Bagasse, the fiber of the cane, for many years burned as a fuel, is now finding use in wall board, as a plastics filler, and as a source of furfural. The mud or settlings from the juices contain the bulk of the wax from the sugar cane. Considerable work on separation and utilization of wax has been done in Louisiana and Mexico (13). Aconitic acid is also being produced from the solids (28).

The final molasses, or blackstrap, has long been a source of ethyl alcohol by the fermentation process. With the advent of synthetic alcohol lessening the demands for blackstrap on the one hand and ion exchange methods lowering the amount of sucrose in the molasses on the other, much wider use of molasses in stock feeds is likely.

Sugar cane has been treated to produce petroleumlike hydrocarbons (9). At temperatures up to 750° F., under pressure and in the presence of alkali, a bituminous product is formed; this is then distilled under vacuum, hydrogenated, solvent extracted, and the bitumin distillate. From this distillation hydrocarbon fractions containing gasoline, middle oil, lubricating oil, and residual asphalt are obtained.

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BREWING

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Filling Beer Kegs from Racker at
Pearl Brewery of San Antonio Brewing
Association

THE origin of beer is one of the lost pages of history. The Chinese, great inventors of an earlier age, are said to have discovered it. The ancient Babylonians, Egyptians, and the Hebrews of the Old Testament had their beer, as did the Greeks and the Romans, each under its own name. We shall never know which low-browed prehistoric man was the first to quench his thirst with a draft of beer brewed in the darkness of some long-forgotten cave. But of this we are certain—the making of beer was one of the first practical experiments ever attempted by man in the field of biochemistry (16).

Whatever its origin, the manufacture of beer has long been considered as an art (1, 11, 17). Not until the middle of the last century did the effect of chemistry as a science begin to make itself felt in brewing, but one brewing expert has been quoted as saying that there is no department of the arts and manufactures where chemistry has exerted a more decided influence than in brewing. In his book on the science of brewing, Hind (6) strikes a compromise between the brewmaster and the chemist when he says that brewing is an art, not a science, but no artist is content to work in the dark to rules laid down by his predecessors. His statement in the introduction to the book is worth repeating:

More than ever I have been impressed during preparation of this book by the wide additions to pure scientific knowledge that have originated in the endeavor to elucidate the mysteries of brewing and perhaps equally, by realization of the inadequacy of our present interpretation of many of them.

Until the middle of the last century American beers were of the top-fermented English type. Because of difficulties in malting and brewing during hot weather due to inadequate refrigeration, manufacturers were quick to adopt German bottom-fermented lager beer introduced in the 1830's. This type beer is completely fermented and undergoes little secondary fermentation on storage; hence it could be stored in cool cellars for hot weather consumption.

In the last 100 years the revolutionizing of the brewing industry has been closely associated with the development of artificial refrigeration and air conditioning for controlled temperatures and

pasteurization to ensure biological stability. Today the place of the chemical laboratory in the breweries of this country is established.

FUNDAMENTAL OPERATIONS

Beer manufacture consists essentially in preparing fermented beverages of a number of types, using barley malt, adjuncts, hops, and water, and fermenting with a bottom fermenting yeast. A typical list of material required for the production of one barrel (a 31.0 gallon barrel is peculiar to the brewing industry) of beer is as follows:

Water, bbl.	
Process	1.25
Utility	10
Barley malt, lb.	36
Adjuncts, lb.	12
Hops, lb.	0.35-0.5
Yeast (as apparent solids), lb.	0.8

Barley was a staple article of food even before wheat, and this partly explains its position as the principal grain used for producing malt. Other contributing factors are its hardness, ease of malting, and ease and completeness of solubles extraction in comparison with other grains. Malt is made by short germination of the grain, softening up the kernel, and increasing the enzymatic activity so important in accomplishing proper inversion in the mashing step.

European brews are generally made from straight barley malt. The old master brewers in Germany had a familiar motto "Hopfen und Malz, Gott erhalts." Simply stated, this means they considered the use of hops and malts as ordained, and any other basic materials were strictly adulterants. In this country, although one brewery, up to last year, made an all-malt beer, the practice is to add a significant proportion of unmalted cereals or adjuncts during the mashing process. Approximately 14 pounds of these adjuncts (largely rice or corn grits or flakes) were used per barrel of beer prior to World War II, and up to 22 pounds during World War II. Corn sugar is also used as one of the adjuncts by some breweries. Schwarz (10) explains that this practice is not in any respect an adulteration but is necessary because of the nature of the malt available and the conditions under which we Americans drink beer. (We judge by both eye and taste, as opposed to German

TRADE GLOSSARY

Adjunct = unmalted grain, sugars, or sirups used in brewing

Attemperation = temperature control

Attenuation = specific gravity reduction

Balling = obsolete density scale; currently used synonymously with degrees Plato

Beer stone = gray-brown deposit of calcium oxalate and organic matter on surface of equipment in prolonged contact with beer

Brewing = all unit processes in beer manufacture beginning with grinding of grain and water treating and concluding with cooling the wort

Brilliance = lack of apparent haze on visual examination

Character = conformance of properties of beer to those of a recognized standard of type

Conversion = general term applied to starch and protein hydrolysis during mashing; specifically the hydrolysis of starch to dextrins, maltose, and glucose

Degrees Plato = a measure of specific gravity of wort; grams of wort solids per 100 grams of wort

Degrees Réaumur (° R.) = a temperature scale invented by René de Réaumur based on the freezing point of water at 0° R. and the boiling point at 80° R.

First Wort = high gravity wort run off the lauter tun immediately after mashing and before sparging

Fullness = palatability as determined by character

Hops = cluster of blossoms of female hop plant, *Humulus lupulus*. Resinous exudate at base of bracts consists of minute granules of lupulin, which contain both bitter and aromatic principles of the hops

Humulon = $C_{21}H_{30}O_{15}$, a bitter constituent of soft resin of lupulin

Kräusen = beer in first stage of vigorous fermentation; foam cover formed during that stage is characteristic

Kuhlschiff = shallow tank for aerating, clarifying, and cooling hot wort after removal of hops

Lautering = extraction of soluble materials from converted mash and separating residual grain from wort. Vessel used variously termed tun, tub, and tank

Lupulin = synonymous with *humulin*. A bright, yellowish-brown granular powder of characteristic odor and hop taste, obtained from *Humulus lupulus*

Lupulon = $C_{26}H_{40}O_4$, a constituent of the soft resin of lupulin

Malting = controlled germination of grain barley to develop enzyme systems and render grain more susceptible to conversion during mashing

Mashing = peptonization, conversion, and arresting of enzyme activity at controlled temperatures

Near Beer = beer containing 0.5 % or less alcohol

Pitching = adding properly prepared yeast to wort to induce fermentation

Premium quality = recognized merit obtained by use of choice materials and complete quality control

Racking = filling barrels with finished beer for consumption

Sparging = spraying hot treated water over converted mash to extract fermentable substances from grain

Trub = precipitated carbohydrate-protein-tannin complexes formed in brew kettle on boiling or in wort on cooling; termed hot break if formed during boiling the wort, cold break if formed during cooling

Wort = unfermented beer; liquid extract after mashing

judgment, for instance, by taste alone.) American barleys have a higher protein content than European. Experience has shown that high protein lager beers with their heavy taste and satiating qualities are not as well suited to the climatic conditions and drinking habits of this country as beers brewed from barley malt plus malt adjuncts. It is difficult, if not impossible, to produce an all-malt beer that is stable from the standpoint of haze formation. In Germany, as beer is ordinarily consumed soon after manufacturing and a brilliant filtered beer is not demanded, the considerations that govern American brewing are not important. At present the American per capita consumption of beer is approximately 17 gallons per year.

Unit steps in beer manufacture may be roughly divided into three areas: brewing, fermenting, and finishing and storage. In the brewing step, starches are converted into dextrins and fermentable sugars; insoluble proteins are converted into soluble forms; and some flavor and aroma are developed. Fermentation converts the sugars to alcohol and small quantities of secondary products of fermentation such as aldehydes and ketones. The finishing step includes carbonation, chillproofing, and aging.

PEARL BREWERY OF SAN ANTONIO BREWING ASSOCIATION

The original plant of the San Antonio Brewing Association's Pearl Brewery was constructed on its present site in San Antonio in 1886 by the late Otto A. Koehler, whose heirs still own and operate the plant. During the "dark days of prohibition," as manufacturers of alcoholic beverages are wont to call them, various portions of the plant were leased for such interests as soft drinks, dairies, and cold storage. The brewing division was retained for production of near beer. Repeal of prohibition in 1933 saw immediate reopening of the plant, and in 1935 fermenting and stock cellars were increased. Finishing cellars were completely rebuilt in 1938, and in 1948 the plant capacity was doubled to 700,000 barrels annually by addition of duplicate equipment items, except the cereal cooker and mash tun. Bottling and racking facilities were expanded in proportion to enlargement of the rest of the plant, and in 1949 a packaging unit for canned beer was installed.

In expanding its facilities Pearl examined more recent advances in equipment; in some units advanced designs were installed and in others the equipment in use was duplicated. Confirming the recognition of the plant of chemistry in the brewing industry, Pearl has one of the most modern control and research labora-

tories, designed by its chemists. One of the top awards for American beers was given to the company at the 1950 fair in Belgium.

Raw Materials

Pearl uses choice brewers' barley malt and, in addition to the general trade specifications for this grade, requires that the malt have a diastatic power in excess of 125 degrees Lintner (500 maltose equivalents) and a bushel weight no greater than 40 pounds. The malt is received in bulk in box cars and is delivered to the malt storage rooms (two frame-lined, one steel) by screw conveyor and bucket elevator. These three rooms have a combined capacity of slightly less than 11,000 bushels. Two continuous reinforced concrete silos (capacity 12,750 bushels each) are under construction for additional malt storage.

Brewers' rice alone is generally used as the adjunct, although when it is not available corn grits or flakes may be used as second preference. This rice is usually first grade polished rice, but consists largely of smaller size broken kernels that do not have the eye appeal of whole grain rice and, therefore, are not packaged by the rice millers. A white, clean rice is required, with protein content as low as possible, oil content of less than 1%, and moisture not greater than 12%. Rice is received in 100-pound bags, and each carload bears a federal inspector's certificate that it is infestation-free. During warm weather the rice is stored in a refrigerated room (36° to 38° F.). Although all temperatures used in this article are expressed in degrees Fahrenheit, the instruments in the plant under discussion, as well as most other breweries, read directly in both degrees Réaumur and Fahrenheit.

Hop growing in the United States is largely limited to the Pacific Northwest and New York. Pearl prefers the fancy Yakima Golding seedless type, grown in Washington State. Hops are purchased on the basis of submitted samples and decisions are dictated largely by physical characteristics. Most important are quantity of lupulin and absence of seeds, leaves, and stems (less than 3% is desirable). Other desirable factors are a high soft (α and β) resin content and very low γ resin. Hops are received in 200-pound bales and stored at 36° F.

As beer is largely water, process water is a major consideration in any brewery. It might be expected that such water would re-

quire no particular treatment other than that ordinarily given to municipal drinking water, but different types of waters are given different treatments, and the same water may be treated differently by adjoining breweries. A treatment proposed by McElroy (7) is indicative of requirements in this regard. The presence of the calcium ion and the sulfate ion is very necessary; calcium precipitates some inorganic and organic phosphates and lowers the pH; it is most desirable as calcium sulfate. Vogel (15) lists some of the beneficial effects of its presence as: aid to gelatinization of the starch, stimulation of enzyme activity, improvement of wort runoff, and flocculation of the break in the kettle, aid to clarification in the cellars, and improvement in stability and flavor of the finished beer.

Presence of calcium as calcium sulfate to the extent of 250 to 300 p.p.m. is optimum. An absence of calcium ion leads to precipitation of calcium oxalate later in the process (with consequent haze) if calcium is introduced from the filter medium during clarification.

The bicarbonate ion is undesirable since it produces a buffer action and tends to give an alkaline mash. Nitrates are undesirable because of possible reduction to nitrite during fermentation, with consequent damage (as an enzyme poison) to the yeast. Presence of sodium and potassium ions magnifies the effect of the hop bitters and in mild beers should be kept at a minimum, except where the sodium ion is present as sodium chloride. Salt is important in the physiology of the yeast cell and in improving the palatability of finished beer.

The pH of water entering the process is important and is carefully adjusted at Pearl within a range of 6.6 to 6.8, after boiling the water to remove carbonate and bicarbonate ions. At least one brewer in this country uses distilled water as process water, adding salts to his own specifications to produce a tailor-made brewing water.

All water at the Pearl Brewery is obtained from private artesian wells, and although already potable, the process water for brewing is treated before use. Table I shows a typical analysis of the untreated water, which has a high bicarbonate content, and of the water after treatment. Lactic acid is added to reduce this alkalinity and additional hardening salts are added in the form of the mixture of calcium sulfate, salt, and other compounds known to the trade as burtonizing salts.

A bottom-fermenting, high attenuating yeast (17E) is employed for fermentation and is obtained in the form of dry compressed cakes of the powdered material. Brewers' yeast is a unicellular organism of the group *Saccharomyces cerevisiae*, selected for beer

fermentation purposes because of its proven ability to produce a beverage of desired characteristics. The yeast is replenished at 6-week intervals, and a new crop is started. Any crop yielding a total bacteria count of 10 or more bacteria per 1000 yeast cells is discarded, even though such a population can normally be tolerated without impairment to fermentation.

Mashing

The barley malt is passed through a perforated cylindrical screen or cleaning reel (Figure 1). Extraneous matter is selectively removed from the screen and an electromagnet removes metallic particles, protecting the mill rollers from damage. The

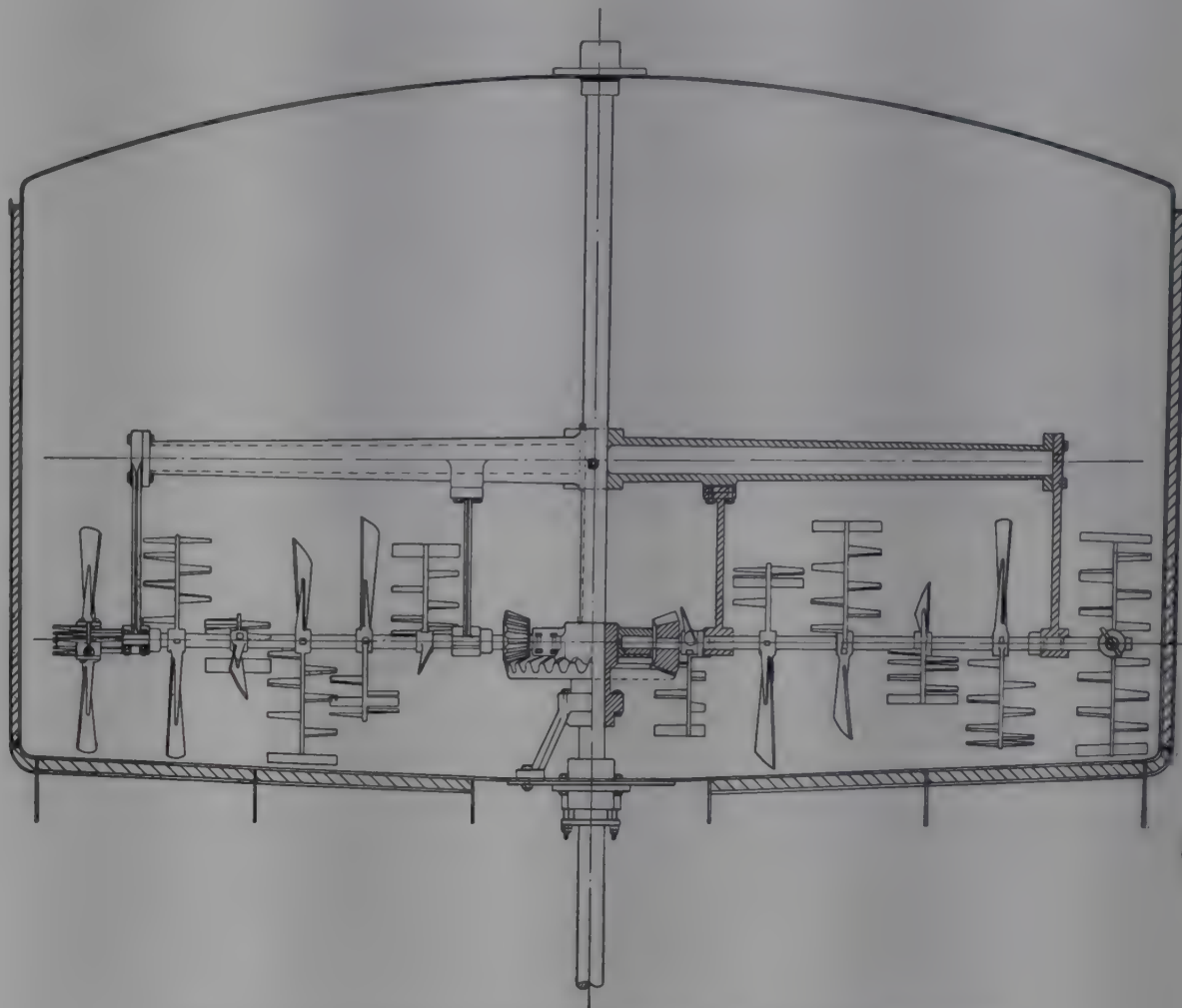


Figure 2. Cross Section of Mash Tun and Agitator

grain is then crushed carefully in a four-roll mill (200 pounds per minute grinding capacity) to break the starch loose from the husk without excessive damage to the husk. The husk can then act as a natural filter bed later in the lauter tun. Successful grinding demands a low moisture content in the grain; 5% or less is desirable, but the grain can be used with as much as 6 to 7%. A higher moisture content than this will result in caking on the mill and poor conversion during mashing.

As the malt is ground it passes into a manually controlled weighing hopper from which it is elevated to the mash tun at the rate of 1000 pounds per minute. The rather interesting conveyor (7E) which accomplishes this elevation is vertical and consists merely of straight prongs on an enclosed endless belt.

The brewers' rice is elevated into a storage hopper, ground on a two-roll mill, and then passes into another storage hopper (400 pounds per minute discharge) from which it is carried by screw conveyor into the cereal cooker. Malt is added to the cooker in a quantity equal to 20% of the weight of the adjunct. Water has already been put in the cooker in the proportion of 1.5 barrels per 100 pounds of cereal adjunct-malt mixture to be used. This cereal cooker is a stainless steel-clad insulated vessel holding 200 barrels. Agitation is accomplished by both a screw-type agitator, about 2 inches from the floor of the cooker and driven from above, and steam nozzles. Steam at 20 to 30 pounds per square inch pressure is injected through silencer-type nozzles (6E) from a steam pipe around the outside circumference of the cooker and about 3 feet from its floor. These nozzles are slanted in order to guide the movement of the material in the same direc-

TABLE I. TYPICAL PROCESS WATER ANALYSIS

Analysis	Parts per Million		
	Raw water	After boiling	After final treatment
Total solids	244.2	149.4	
Loss on ignition	106.6	52.6	
Silica (as SiO ₂)	4.2	5.4	
Fe	0.05	0.1	
Ca (as CaO)	81.5	14.2	
Mg (as MgO)	23.5	12.1	
Sulfates	10.5	29.0	
Free CO ₂ (as CaCO ₃)	9.3	...	
Alkalinity			
Bicarbonate	207.2	94.7	
Carbonate	...	8.2	
Probable combination			
Na ₂ SO ₄	18.8	51.1	
CaCO ₃	145.3	25.3	
MgCO ₃	49.1	25.6	
Na ₂ CO ₃	3.9	46.3	
NaCl	23.1	32.3	125.0
CaSO ₄	275.0
pH	7.7	8.2	6.6
pH after laboratory boiling	9.2	8.5	...

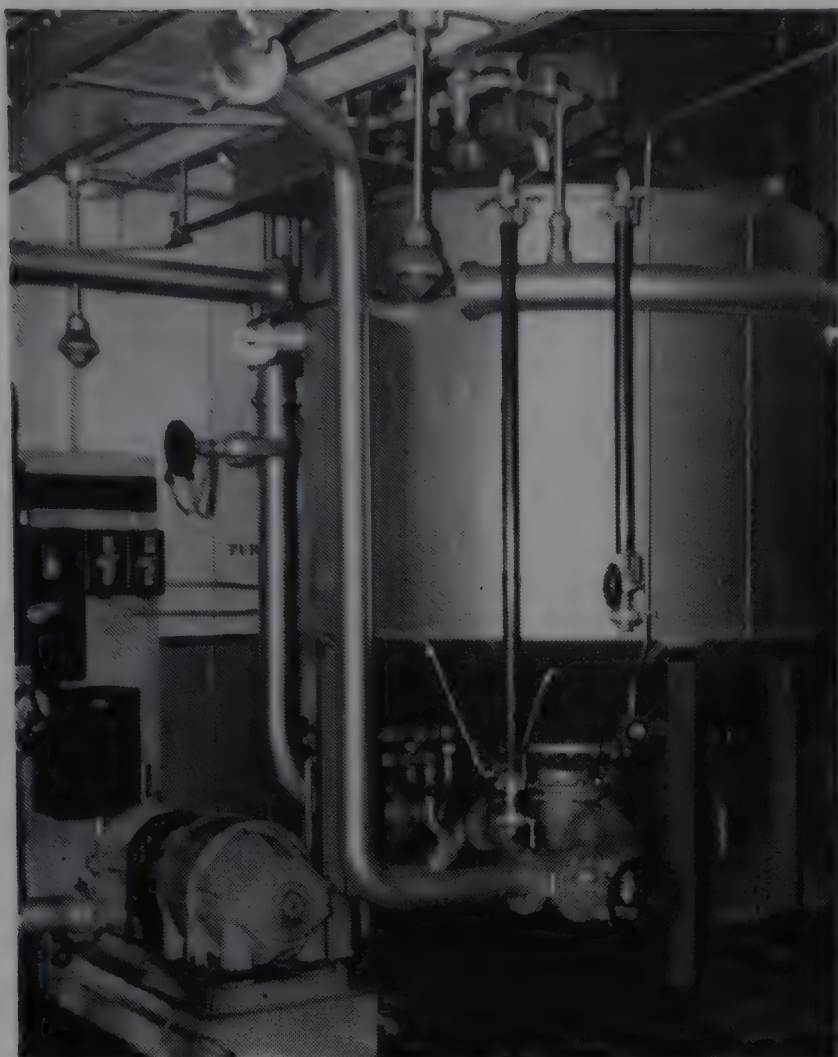


Figure 3. New Type Hop Jack

tion as the agitator motion. Spiral baffle plates on the walls of the cooker also aid in thorough mixing.

The mixed cereals and water are elevated to 158° F., held for 15 minutes at that temperature, then heated to boiling and cooked for 30 to 45 minutes. Cooking the adjuncts prior to the mashing step accomplishes solubilization of the starches; the main reason for adding the small quantity of mash to the adjuncts and resting at 158° F. has been the belief that this procedure accelerates solubilizing. Actually, this may not be entirely correct (and therefore some brewers cook their adjuncts alone initially), but presence of the malt husks aids in transfer of the liquid after solubilizing.

While the adjuncts are being cooked, the main portion of malt is infused with warm (104° to 113° F.) water. This water, in the ratio of 1 barrel of water to 100 pounds of malt, is put into the 300-barrel stainless steel-clad, insulated mash tank or tun (15E); malt is then added and thoroughly mixed with the water, and infusion is carried out for 30 to 60 minutes. Time and temperature of infusion varies in different breweries depending on the type malt used, but during this period the temperature is maintained constant, and there is no agitation. Among the reactions accomplished by infusion are the lactic acid rest, or acidification of the mash, and conversion of high molecular weight proteins into those of lower molecular weight.

The mash tun agitator consists of blades mounted spirally around a central horizontal shaft (Figure 2). This shaft rotates about its own axis and also about a vertical shaft in the center of the cooker, to which it is attached. The cereal cook is so timed that the end of the boiling period coincides with the end of infusion time of the mash. The mash tun agitator is started at full speed (12 r.p.m.), and the cooked adjuncts are pumped into the main mash at such a rate that the mash temperature is raised approximately 2.8° F. per minute to the temperature desired for conversion. This temperature ranges from 154° to 162° F. depending on the degree of attenuation desired and the diastatic activity of the malt. In this transfer of adjuncts a high capacity stainless steel pump (1E) empties the cooker in 10 minutes, and additional heat is supplied to the mash tun by means of live steam. Some brewers prefer horizontal cylindrical mash tuns, particularly where space may be a limiting factor.

The mashing process is essentially the saccharification of starch by the diastase enzyme, resulting in dextrins, maltose and glu-

cose. The diastatic activity of the malt is sufficient to invert not only the malt starches themselves but also the starches in the adjuncts. Complete inversion of the starch is imperative. Most of the action of the proteolytic enzyme peptase has already taken place in the malting process, but proceeds to a limited extent also during mashing. Complete breaking down of the protein, however, is not possible, nor is it desirable. Part of the protein is lost in the grain residue as insoluble, part of the soluble protein is removed in the kettle as a protein-tannin complex precipitate, part is consumed as yeast food, and the rest remains in the beer as soluble protein.

The operator follows the progress of conversion in the mash by the simple and conventional iodine test for starch; 20 to 30 minutes are usually required for the conversion. Satisfactory completion is indicated by complete disappearance of the blue color in the starch test. When conversion is completed the temperature is raised to 167° F. to inactivate the enzymes. The mash then drops by gravity into one of the two 300-barrel stainless steel-clad, insulated vessels (10E, 15E), termed lauter tuns. Each vessel is equipped with an agitator consisting of a horizontal bar revolving around a central shaft. Vertical blades or "lauter" knives mounted with pitched projections are mounted on this bar, and the agitator can be raised or lowered hydraulically.

The lauter tuns have false bottoms containing staggered parallel perforations 0.0625×1 inch. Sufficient water is added to cover the false bottoms, and just enough live steam is added, through outlets similar to those in the cereal cooker, to heat the walls of the vessel. After the mash is dropped the agitator is started slowly (10 to 12 r.p.m.) to effect even distribution of the mash. The speed is then reduced to 0.33 r.p.m. and hot water is forced upward into the lauter tun through the runout pipes to flush out the material around the false-bottom openings. The blades are then stopped, raised out of the mash, and the runoff pipe valves closed. The entire mash then rests for 30 minutes.

The runoff system consists of a series of concentric copper pipes on the outside of the bottom of the lauter tun and connected to the bottom of the vessel by means of a large number of short 1.5-inch nipples. Each concentric ring flows into a central header, which empties into a large copper basin ("Grant"). Piping is so arranged that wort may be pumped from this basin back into the top of the lauter tun until it runs brilliant, at which time it flows to the brew kettles.

After the mash has rested, the inlet valve to the grant is opened slowly and hazy wort is pumped back into the lauter tun. The operator determines by visual inspection when the wort is sufficiently clear to be collected in the brew kettle. From 15 to 20 minutes are usually required for this operation. The first wort (approximately 35% of the total volume of final wort) is then allowed to flow by gravity or is steam pumped into the brew kettle, depending on which lauter tun is used. Piping is also arranged so that wort may be collected in a 10-barrel copper vessel for use as yeast food ("Würze").

When the first wort has been drained off into the kettles the grain and husks remain in a mass on the perforated false bottom. Since they are saturated with wort, they must be extracted with water to recover the solubles. The agitator is lowered so that it just cuts the surface of the grain and is rotated very slowly (0.33 r.p.m.) to prevent packing and to permit good extraction. Hot water is sparged over the surface of the grain from a perforated copper pipe revolving at the top of the lauter tun. Temperature of this water is controlled so that mash temperature during sparging is within 156° to 167° F. Higher temperatures result in an extraction of harsh, bitter principles from the husks which have an adverse effect on the flavor of the finished beer. Lower temperatures reduce the efficiency of extraction of the solubles and favor undesirable drastic enzyme activity.

Operators in some breweries employ a technique known as "mashing up" in order to facilitate handling of this sparging and

extraction step. It consists essentially in backwashing the lauter tun with high pressure sparge water and, at the same time, operating the agitator at low speed and fully down. The mash is then rested for 20 to 30 minutes, and the standard lautering procedure is carried out.

The process of extraction is followed with a hydrometer, and wort is run off to the kettles until the solids content is down to 1° Plato. Total time required for runoff is 3.5 to 4 hours. The grain residues are reduced with water to a consistency enabling them to be pumped (16E) through a 6-inch line into two cone-bottomed collecting vessels each large enough to contain the residues of two brews. This grain, in considerable demand by local dairymen, is sold on contract as is in the tank to a local distributor for sale as dairy feed.

In any mashing process, the composition of the wort at the end of mashing depends on the type and amount of malt and adjuncts, the way these are crushed, the amount and type water used, variations in time and temperature, and techniques used in the lautering and runoff step. Some smaller breweries use combination mash and lauter tubs. The most recent change in techniques has been substitution of filter presses for lauter tuns. Outstanding advantages claimed for filter presses are increased speed of handling and higher yield. On the other hand, considerably more capital investment may be involved, and some brewers insist that a harsh husk flavor, not encountered by using lauter tuns, results when mash filters are employed.

Brew Kettles

The two 400-barrel brew kettles at Pearl (5E, 10E) are constructed of 0.25-inch copper. These are heated by a steam coil on the floor of the kettle and a percolator type steam heater in the center. The wort flows from the grant into the kettles until it just covers the coil. At that time steam flow is adjusted so that the temperature of the wort begins to rise slowly. When the percolator is entirely covered with wort, steam to the coil is turned off and percolator steam (25 to 30 pounds per square inch pressure) is turned on to give the same rate of heating. This rate is adjusted so that when the kettle is slightly more than half full (200 to 250 barrels) the boiling point is reached. At this point the first hops are added, and boiling is continued at an even ebullition rate for 135 minutes. Further addition of hops is at definite hopping intervals to give a constant bittering value (or soft resin content) as determined by previous analysis of the hops. Total amount of hops added is from 0.35 to 0.5 pound per barrel of finished beer; this varies somewhat according to type of hops used, time of boiling, and similar factors.

In general, objectives to be reached in the brew kettle are accomplished by boiling and hopping. Boiling aids in coagulating proteins which might cause difficulty in producing a clear finished beer, sterilizes the wort and destroys enzymes, and concentrates the wort. Hopping, besides imparting aromatic and flavor qualities, aids in protein coagulation by formation of protein-tannin complexes and has preservative qualities which help stabilize the beer. The hop acids are particularly effective in inhibiting the growth of Gram-positive organisms. Rabak (9) in a recent article, discusses the use and function of hops in brewing.

Time of boiling in the kettles at Pearl is within the range 2 to 2.5 hours and is ended according to a predetermined time schedule. In an effort to complete the precipitation of proteins of low solubility in the kettles, some brewers add designed materials (essentially tannic acid, sulfites, and related compounds) for this purpose. In so doing, they also reduce considerably the time necessary for boiling. During boiling the hot break occurs. This is a striking formation of a flocculent mass of coagulated protein. Most brewmasters view a good hot break as indicative of success in the mashing and boiling operation. Actually, this is controversial and most chemists, on the other hand, consider brilliance in finishing as the most important evidence of successful brewing and not necessarily related to hot and/or cold breaks.

When boiling is completed, it is important to remove the wort

from contact with the hops as quickly as possible to avoid an excess of hop principles in the beer. The wort flows by gravity to one of two hop jacks, each interconnected with both the kettles. The older type is a rectangular tank holding 200 barrels. A portion of the upper half of the hop jack is occupied by a rectangular strainer, and the wort passes through this strainer and into the bottom of the tank. Some of the coagulated protein or "Trub" separates out at this point. Finally, water at 167° F. is sparged over the tops of the hops on the strainer to remove residual wort. In order to prevent excessive dilution of the wort, the volume of this wash water is fixed at 1 barrel of water to 15 pounds of hops. The hops are dried and used for soil conditioning.

The new type hop jack (15E) installed by Pearl is a mechanical strainer consisting essentially of two concentric cone-bottomed cylinders with 75-barrel capacity (Figure 3). The hops and wort flow into the inner cylinder, on which a slight pressure is maintained, and the wort passes through perforations into the outer cylinder, while the hops are retained. After sparging a special outlet in the inner cylinder is opened, and the hops are flushed out with water. Each type hop jack has its respective advantages. The new type processes 375 barrels in 30 minutes, but the advantage of removing the wort from the hops in 15 minutes as can be done in the old type must not be overlooked. Space requirements of the new type are about 20% that of the old and mechanical removal of the hops is an advantage. The old type does not require close watch by an operator, however, whereas the new does. Cleanup time for both types is about the same.

Cooling of the hot wort is an important step because of the dangers of infection. Different methods are used depending on the individual brewery, its location, space requirements, and cost considerations. The more recent techniques employ a hot wort tank followed by enclosed double-pipe coolers and plate-type heat exchangers. These reduce considerably the attention which must be paid to maintenance of strict sanitary conditions in the cooler rooms, but still require air introduced for the subsequent fermentation step to be sterile. Efficiency of heat transfer is excellent and the exchangers are well suited to limited space requirements. These advantages are somewhat offset, however, by high initial investment costs.

Pearl, like many other breweries, has retained the surface cooler or "Kuhlschiff" and uses the vertical Baudelot cooler in conjunction with it. Careful attention to maintenance of sanitary conditions (industrial air pollution problems are almost nonexistent in San Antonio) enables cooling to be carried out with satisfactory efficiencies and at low cost. Therefore, when installing additional cooling facilities, Pearl decided to duplicate its Baudelot equipment rather than install closed coolers.

The hot wort is pumped to a shallow rectangular stainless steel-clad tank or kuhlschiff large enough to hold two brews. This tank is in a closed room at the top of the brewery. The bottom of the tank is slightly sloped to the side, where an outlet valve is located; the ceiling of the room is vaulted to prevent droplets of condensed water vapor from falling into the tank. A special paint (11E) is used on the walls.

While resting in the kuhlschiff, the temperature of the wort drops to between 178° and 190° F., and additional trub settles out on the bottom. The wort is then decanted through a strainer in the side of the tank and drops by gravity to the header of a Baudelot cooler (15E). This cooler, consists of a series of 2-inch horizontal tubes arranged in vertical stands. The 48 upper tubes of the new cooler are copper and carry water at 77° F.; the 32 lower ones are stainless steel carrying liquid ammonia. In the old cooler there are 52 copper tubes and 20 varnished iron tubes. A trough at the top of the cooler distributes the wort over the tubes, and as it runs down the outside into a receiving pan at the bottom it is cooled to 50° F. From the cooler pan the cooled wort flows into open starting tanks.

The cooler room is entirely closed, with double doors, and has forced air circulation. A positive pressure of approximately 1 inch of water is maintained, and dry air at 77° F. enters the room through a double bank of glass floss filters (9E). Such filtration is necessary to prevent contamination of the wort by micro-



Figure 4. Line of Tanks in Finishing Cellars

organisms in the air. A small exhaust fan is located at the opposite end of the room. The windows are amber glass (similar in transmittance to the conventional beer bottle) to reduce the oxidative effects of light. The walls of the room are very smooth to eliminate crevices which could harbor nutrients favorable to biological growth.

Fermentation

The wort in the starting tanks is now ready for addition of yeast for fermenting, to convert the sugars produced in the mashing step into alcohols and small quantities of various oxidation products (aldehydes and ketones, and other compounds). All fermenting tanks (14E) are glass-lined (3E), and the twelve starting tanks are rectangular open tanks each having a capacity of 385 barrels of wort. All recirculated and fresh air coming into the fermentation cellars is filtered through a bank of air filters, and in each air circulating duct a double bank of ultraviolet lamps (18E) is so placed that the air is sterilized, but the light rays do not strike the fermenting wort. With the advent of refrigeration and air conditioning the term "cellar" is generally a misnomer in the brewing industry, since the tanks need no longer be underground to ensure uniform temperatures. There is considerable controversy in industry over the efficiency of ultraviolet lamps for air sterilization. However, repeated tests in Pearl's laboratory show a marked reduction in total amount of bacteria per cubic foot of air when ultraviolet lamps are in use. It is imperative the air velocity-volume to radiation ratio be properly adjusted and that the tubes be kept clean in order that radiation not be reduced. The lamp tubes are mounted on sliding trays so that they can be slipped out easily for weekly cleaning. Because of the retrograde efficiency versus time curve, the individual lamps are replaced at 6-month intervals.

The various brews as cooled are divided in such a manner that all yeast pitching can be accomplished in an 8-hour working day. Brews made at night, then, are simply put into the fermenting tanks on top of those already pitched. Yeast is collected regularly in a stainless steel yeast collecting tub, but settling is accomplished from a brew of completely fermented beer which is specially handled to yield a good crop of viable yeast. During

one fermentation cycle a multiplication rate of three to four times the amount of original yeast is obtained.

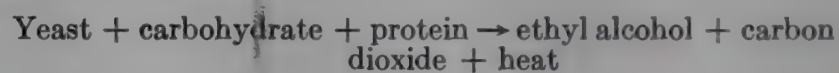
Yeast, mixed with wort in a 1:1 ratio in a 10-barrel stainless steel tank, is passed through a fine copper wire strainer to remove any trub that might be present and is incorporated with wort to approximately 8 barrels of liquid. The mixture is then roused by repeatedly dipping up a portion and dropping it from a height back into the liquid. This aerates the medium and mechanically separates the yeast cells from each other. Both air and cell surface are important factors in the metabolism of the yeast cell.

The yeast-wort suspension is pumped into the starting tanks containing the various worts. During the pumping operation air is bubbled into the wort at 15 to 20 pounds per square inch pressure through pear shaped nozzles (1) to aerate the wort completely and (2) to distribute the yeast throughout the entire brew. After this introduction, air is excluded from contact with the brew during the remainder of fermentation and finishing steps.

Within 20 to 24 hours the first stage of vigorous fermentation known as the "*Kräusen*" stage occurs. This stage is characterized by a thick, creamy foam on the surface of the wort. As fermentation continues this develops into thick curls, the volume of foam increases, and the carbon dioxide released in the fermentation reaction breaks through.

At this point the fermenting beer is transferred to 180-barrel vertical cylindrical closed fermenting tanks. All pumps (1E) used in transferring beer are brass. The head space in these closed tanks is held to a minimum in order that air above the surface of the fermenting beer may be quickly flushed out by the carbon dioxide evolved. Pressure is allowed to build up to 4 or 5 pounds per square inch gage, and the evolving gas is exhausted from the tanks until its purity reaches 99.95% carbon dioxide as determined by laboratory analysis. It is then collected, compressed at 275 pounds per square inch, and stored as a source of supply for later carbonating steps. Safety valves are provided on all tanks to prevent excessive pressures. Carbon dioxide can be collected economically for 3 to 4 days.

Fermentation is a metabolic process and may be expressed most simply by the statement:



Michaelis (8) and Siebel (12) some years ago discussed in detail in a brewing symposium the various oxidation problems involved in fermentation. Temperature of the fermenting beer is never allowed to exceed 57° F., in order to obtain consistent fermentations. If this is not done, attenuation cannot be carefully controlled, by-products having an adverse effect on flavor and aroma are formed, and the finished beer is susceptible to infection and high attenuation. Hence all fermenting vessels are equipped with copper cooling coils or attenuators refrigerated with brine at 25° to 30° F., and the fermenting cellars themselves are refrigerated (45° F.). Recording thermometers are used throughout the plant. In one of the newest British plants (4) a stainless steel trunnioned attenuator has been installed. One of its main advantages is that it can be swung around, enabling easy cleaning both of the attenuator and the fermenting vessel.

After 3 or 4 days in the closed fermenting tanks a portion of the beer is transferred to 380-barrel yeast collecting tanks, where it is rapidly chilled to the range 36° to 39° F. During this time the yeast flocculates and settles to the bottom of the tank. Any foam that forms on the surface of the beer is skimmed off, since this foam contains bitter hop residues and weak and dead yeast cells. After the yeast has settled (5 to 6 days) the beer is decanted. The yeast, which remains as a mat about 4 inches thick on the bottom of the tank, is stirred carefully and skimmed with a wooden creel to remove residual beer and a very thin layer of yeast. The yeast is then mixed thoroughly without whipping and pulled out into stainless steel buckets. The apparent solids content is determined by the laboratory, and the operator is then advised of the proper number of pounds of yeast to pitch.

The progress of fermentation is followed closely by temperature and attenuation checks. Table II shows pH and attenuation changes throughout the steps in beer manufacture.

TABLE II. ATTENUATION AND pH CHANGES DURING BEER MANUFACTURE

	pH	Apparent Degree of Attenuation, %
Water	6.6	...
Mash	5.6	...
First wort	5.5	(18° Plato)
Wort tailings	5.6	(1° Plato)
Cooling stage	5.6	...
Fermentation, hours		
24	5.2	13.0
72	4.6	42.8
96	...	61.0
144	...	71.3
Rest (in ruh cellars)	4.4	83.0

Temperatures are read twice daily by the brewmaster or his assistant and recorded directly on the tank by the laboratory after the fourth day. When the required degree of attenuation is attained, the brine flow through the cooling coils is increased at a rate calculated to lower the temperature of the beer 0.45° F. per hour at the beginning; the rate of cooling is reduced as the temperature is dropped to a final 36° to 39° F. The beer is then passed through coolers (4E) where it is brought to a temperature of 32° to 34° F.; it is then ready for finishing. The beer from the yeast collecting tank is treated in a similar manner.

Finishing

The completely fermented beer is blended for attenuation characteristics and alcohol content and is transferred to 300-barrel vertical cylindrical glass-lined tanks (3E, 14E) in rooms known as "Ruh" cellars or rest cellars. In the transfer from the fermenting to the ruh cellars, the beer is carbonated slightly through a carbonating arm (19E) which injects carbon dioxide directly into the beer as it passes through the pump. The ruh cellars are each complete units in themselves, closed and with individual refrigerating units which maintain them at 32° F. (freezing point of beer is approximately 28° F.). All tanks in the brewery have individual gages and those in the ruh and finishing cellars are equipped with manometer-type gages. In the ruh cellars yeast and other material settle out, and certain taste characteristics are developed. This is attributed to ester formation, indirectly confirmed by the fact that during the ruh stage there is a slight but nonetheless uniform decrease in the alcohol content of the beer.

Following storage in the ruh cellars, the beer is pumped into the finishing cellars. (Some brewers prefer to carbonate at this point in saturators or tanks, where beer flowing downward is contacted by a stream of carbon dioxide, rather than by partially carbonating at each pumping step and completing the process in the finishing tanks.) During this pumping operation the beer is clarified by filtering through pressure filters (20E), capacity 110 barrels per hour each. The plates of the filters have nylon screens and are precoated with diatomaceous earth. Cedar chips were used for clarifying prior to the introduction of pressure filtration and are still in use by one large brewer. Isinglas is also used as an aid to filtration by some brewers.

Additional carbonation is carried out at the pump, temperature is maintained at 32° F. during transfer, and a proteolytic enzyme is slurried into the beer as it is pumped into the finishing tanks. Typical enzymatic material of this kind may include either pepsin and a bacterial enzymatic material or a proteolytic enzyme of animal or plant origin combined with a metabolic material (enzymes) produced by the cultivation of molds (18). A number of enzymatic compositions are available from different manufacturers. The particular type used at Pearl (17E) contains a mixture of a number of enzymes including a purified and

standardized proteolytic enzyme of plant origin of the papain type. This compound is supplied in powdered form containing a soluble diluent for purposes of standardization and is adjusted by the manufacturer to facilitate handling. The material is used at a rate up to about 2 pounds per 100 barrels of beer, depending on the individual characteristics of the beer and the degree of chill haze protection desired.

Some breweries prefer compounds containing pepsin to papain. What is known as chill haze in beer is due to the presence of colloiddally suspended proteins and precipitated proteins formed on rechilling or excessively chilling the packaged beer. Both papain and pepsin peptonize proteins or catalyze depolymerization through hydrolysis. It is generally agreed that papain catalyzes depolymerization of proteins at the isoelectric point, whereas pepsin catalyzes protonated proteins, but this important difference is sometimes overlooked even by chemists. Since the enzyme is added at 32° F., the maximum concentration of the proteins would be expected to be in solution; apparently two things take place with the addition of papain:

1. Depolymerization of native proteins, resulting in more soluble peptones and polypeptides and therefore a more stable solution of the proteins.
2. Depolymerization of the protein fraction of tannin-protein complexes, resulting in more soluble polypeptides and/or peptones and a new tannin-protein complex with an isoelectric point higher than the pH of the beer.

The complex then precipitates out, leaving a stable solution, as evidenced by the precipitate formed in brilliantly filtered beer when treated with papain. Keg beer does not receive chillproofing since it is normally consumed within a short time and is not generally subjected to excessive chilling.

Control of oxidation and elimination of oxygen after the fermentation and in the finishing process are important in the prevention of oxidation haze. Some investigators believe this is accomplished by a change in rH. To retard the development of oxidation haze, elimination of oxygen after fermentation and during finishing is generally relied on as an effective treatment.

Beer remains in the finishing tanks (300- to 625-barrel capacity) shown in Figure 4, for a period of 10 to 14 days. During the early part of this storage period the beer is completely carbonated to a level of 2.7 volumes of carbon dioxide per volume of beer. This is accomplished by introducing carbon dioxide at 20 to 25 pounds per square inch pressure through porous clay cylinders (20E) in permanent sockets attached to the tank bottoms.

When ready for packaging the beer is filtered through pulp filters (8E) consisting essentially of cotton fibers and asbestos. After each filtration this "Filtermass" is removed, mangled, and washed in clear, warm water, then bleached and sterilized at 160° to 180° F. with chlorine. The washed pulp then goes directly to a pad-forming machine where it is compressed at 80 to 90 pounds per square inch to form new filter pads. Advantages and disadvantages of this type of filtration, as well as the diatomaceous earth filters are discussed by de Clerck (3).

Keg beer is pumped through a government meter (2E) directly to the racking machine (title photo) from which the kegs are filled immediately. This machine consists of a horizontal steel cylinder to which the filling arms are connected. A counter pressure of 15 to 20 pounds per square inch is put on the keg and then beer is allowed to flow in. The bung is put in place by hand and kegs are stored in a refrigerated (32° F.) room.

Beer for bottling is pumped, also through a government meter (13E), into bottle storage (essentially a surge tank), termed "government cellar." At the Pearl Brewery, the bottle house is 200 feet from the finishing cellars. To prevent wild or foaming beer prior to or during the bottling operation the government cellar is located immediately below the bottle house. Thus the beer has the minimum distance to travel into the bottling machines directly above.

TABLE III. EQUIPMENT CLEANING SCHEDULE

Item	Method	Frequency
Grain storage bins	Empty, clean, and gas with tear gas (chloropierin, 99%)	2- to 3-week intervals
Water treatment tanks	Empty and clean completely	After each 2500 barrels of water treated
Mash tun and cereal cooker	Varnish	Annually
Lauter tun; grant	Scrub with broom and hot water	After each brew
Brew kettles	Polish inside and out	Weekly
	Scrub with broom, hot water, and detergent	After each brew
	Clean with caustic soda; polish inside and out	Each week-end
Hop jack	Scrub with broom and hot water	After each brew
Kuhlschiff and connections	Scrub with broom and hot water	After each brew
Wort lines	Clean with caustic soda	Each week-end
	Flush with live steam	Before each brew
	Flush with water	After each brew
	Fill with 10 to 15% caustic	Each week-end
Cooler coils and pans	Clean with antiseptic solution and hot water	After each brew
	Clean with 15 to 20% caustic	Twice each week
Wort headers (on coolers)	Polish	Weekly
	Flush with steam	Before each brew
	Dismantle and clean separately with caustic	Weekly
All tanks	Scrub with water, followed by high free-chlorine solution; sweep or allow to drain dry; remove beer stone (calcium oxalate) with sulfuric acid	After each use
Beer lines	Flush thoroughly with water	Before and after use
	Circulate 5 to 10% caustic for 2 to 2.5 hours	Weekly
Filters	Wash down with water	After each use
Cellar floors	Spray with chlorine solution	Daily
	Scrub with caustic soda-lime mixture; spray with chlorine solution	2- to 3-week intervals
Valves, couplings, fittings	Wash with water	Before and after use
	Soak in antiseptic solution	Weekly
Yeast utensils (buckets, tubs, etc.)	Completely dismantle and clean	Daily
	Clean with antiseptic solution (wooden creels are never allowed to develop frayed or worn edges)	Before and after each use
Ultraviolet lights	Remove from sockets; wipe with alcohol	Weekly
Floss glass filters	Change	3 weeks maximum or earlier as indicated by bacterial cultures
Lamsen stones	Water at 50 pounds per square inch pressure; then steam at 5 pounds per square inch pressure	After each use
Racking machine	Completely dismantle and wash with antiseptic solution	Before and after use
Fillers, crowners, labelers	Wash with hot water, detergent, treat with live steam	After each use
Pasteurizers	Clean partially	Daily
	Drain completely and clean	Weekly
Kege	Wash with hot water and steam	On return and re-use
Bottles	Wash in successive solutions of 5, 4, and 3% caustic soda	On return and re-use
Cans	Steam and cold water wash	Before filling
Cases	Clean manually; insert new partitions when necessary	After each use

CLEANING OPERATIONS

As beer is brewed for beverage purposes, brewing must be accompanied by the most exacting cleanliness requirements. However, the average chemist or chemical engineer, not in direct contact with the food and drink industry, probably does not realize the extent to which cleaning operations play a part in the modern brewery. In fact, they are an important one of the triumvirate of factors which constitute a byword among brewers: time, temperature, and cleanliness. No compromises are tolerated in

the matter of cleanliness. When even a small amount of yeast or other material is spilled on the floor it is immediately cleaned.

Table III shows the San Antonio Brewing Association's complete cleaning schedule. All vessels in the plant are sterilized after each use. All tanks, in addition to mechanical cleaning, are rendered sterile by use of antiseptic solutions applied with a brush. They are then swept until completely dry. All air required to be sterile passes before use through two scrubbers containing 5% potassium permanganate. Ultraviolet lamps used extensively for air purification are very effective in reducing bacteria count.

Many of the cleaning procedures require the use of caustic soda and putting solid caustic soda into solution continually posed extra labor requirements and hazards. Therefore, Pearl has installed a mild steel, 18,000-gallon tank, purchases liquid caustic (50%) in tank car quantities, and simply dilutes it as needed. Pearl was one of the first breweries in this country to adopt such a method (quite common in other parts of the chemical industry); others have since adopted this technique of handling. As a result, liquid caustic is always available; it is easier to handle than the flake, is more economical because shipping costs are less, and less inventory and storage space are required.

LABORATORY

Pearl maintains what is probably the most modern and complete brewing laboratory in the South. High precision equipment is available for performing all standard analyses of beer, brewing materials, chemicals, and other materials purchased on specification basis. The laboratory is directly responsible to the general manager and works in close cooperation with department chiefs to maintain quality and uniformity.

TABLE IV. ANALYSIS OF AN INDIVIDUAL BEER

Color, ° Lovibond	3.00
Optical density, 430 mμ, 10 mm. cell	0.20
Sp. gr., 20/20° C.	1.01175
Apparent extract	3.00
Alcohol	
Wt. %	3.50
Vol. %	4.49
Real extract	4.61
Original ° Plato	11.5
Degree of fermentation	
Real	65.7
Apparent	81.3
Iodine reaction	Negative
Total acids (as lactic acid), %	0.14
Protein, wt. %	0.34
pH	4.4
rH (I.T.T. ^a)	200
Reducing sugars (as maltose), %	1.20
Ash, %	0.16
Air, ml.	1.00
Foam retention, Sigma	120.0
Surface tension, dynes/cm.	43.0
CO ₂ , volumes	2.70
Iron, p.p.m.	0.10

^a Indicator time test.

Control analyses may include not only those on beer, but also a variety of activities from biological examination of air to determination of the physical strength of paper beer cups. Table IV gives the analysis of an individual beer, showing the typical determinations performed. Spot tests and semimicrochemical methods are employed wherever possible. Determinations of metal ions are one of the most frequent analyses, with carbon dioxide volume and purity and air content, respectively, the second and third most important determinations.

Although the greater portion of laboratory activity is of necessity devoted to control work, definite attention is paid to research and development projects. Mention has already been made of the change from flake to liquid caustic soda; the laboratory played a large part in developing this method. Other projects have resulted in the development of a modification (19) of the Monier-Williams method for sulfur dioxide determination and a method for determination of sulfates in beer. A long-range research program is in progress for studying the maximum density of different beers. Object of this study is the derivation of an Ostwald-type equation for predicting the temperature of

maximum density, using values obtainable from several simple analytical determinations.

The importance of biological control has been pointed out. A large number of cultures and microscopic examinations are made daily in accordance with a planned program. All pitching yeast is examined microscopically before each pitching, and an apparent solids content determination is made. A program is just being put into effect for culturing certain generations of pitching yeast on special media (5). This method is designed to supplement routine microscopic examination; small variations in biological population are more readily recognizable.

FUTURE PROSPECTS

The brewing industry in general is very proud of its products and the manner in which they are manufactured. Most breweries welcome visitors, particularly those in the chemical field.

As far as future prospects for changes and improvements are concerned, it must be remembered that the modern American brewing industry is essentially only 18 years old, although a number of important advances were made by Americans (use of commercial enzymes, modern malting procedures, and improvements in closures) before prohibition. Brewing technology is just beginning to develop, particularly in regard to the application of chemical engineering design to its operation. Progress will be slow because every brewmaster and brewing chemist is aware that he is dealing not only with predictable chemical reactions but also with so-far unpredictable biochemical changes. In the future he will probably draw more and more heavily on the work of the bacteriologist and geneticist.

Breeding of new improved strains of barley takes a long time, and the Barley Improvement Committee of the Malt Research Institute has had a long term research program underway for the past 10 years.

The liquor industry sometimes wonders why brewers find it necessary to boil the wort and hops together in the brew kettle. Extraction of hop principles and injection of the liquid extract into cold beer seems to them a better way of accomplishing the same results. Some breweries do add hop extracts to their finished beer, but that does not solve the problem entirely because the wort must still have been boiled to coagulate proteins. Until a more satisfactory answer is found, most brewers will probably stick to the proven technique of adding hops direct to the kettle.

A dozen years ago Sippel (13) said that the brewing industry should take the lead in encouraging and stimulating the growth of American hops of definite characteristics, with the trend toward seedless hops certainly in the right direction. He also challenged the research worker on the possibility of continuous mashing and brewing techniques and the application of pressure kettles in brewing. An approach to a continuous process is being made by one of the large breweries in this country, but the biggest obstacle lies in the fermentation step, where continuous production would result in excessive residual sugar content and lead to an unstable beer.

Instrumentation, as the chemical process industries know it, is still in its infancy in brewing. Slater (14) recently described two basic instrument developments that, if adopted widely, will do much to put breweries on a level with more highly engineered chemical and food processing plants. One of these is the time-pattern instrument combination, enabling automatic regulation of a process variable over a definite predetermined time schedule. This program is applicable to malting, mashing, and fermentation. Electronic instrumentation is applicable to control of process water pH and to coordinated process analysis.

Another fertile research field for the brewing chemist is in the aging process, where little chemical or bacteriological information has been obtained.

Brewers are always on the lookout for improvements in cleaning techniques; the San Antonio Brewing Association is carrying out experiments in actually preventing the formation of beer stone (calcium oxalate). Each time a tank is cleaned a solution of gluconic acid (12E) is applied and allowed to remain in contact with the inside wall for varying periods of time. Beer stone formation theoretically should be prevented through a sequestering action.

For bridging the gap between laboratory scale and commercial brewing in evaluating brewing materials and processes for future improvements, Brenner (2) has described 2- and 5-gallon pilot plants.

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- (11E) Master Mechanics Co., Cleveland, Ohio, Masterkote Sanitile paint.
- (12E) Pfizer, Charles and Son Co., 630 Flushing Ave., Brooklyn 6, N. Y., gluconic acid.
- (13E) Pittsburgh Equitable Meter Co., Pittsburgh, Pa., fluid meters.
- (14E) San Antonio Machine and Supply Co., San Antonio, Tex., fermenting and finishing tanks.
- (15E) Schock-Gusmer & Co., Inc., Hoboken, N. J., mash tuns, valley-bottom lauter tuns, wort coolers, mechanical hop strainers.
- (16E) Taber Pump Co., 283 Elm St., Buffalo 3, N. Y., size 60 grain pump, 20-hp. drive.
- (17E) Wallerstein Co., Inc., 180 Madison St., New York 16, N. Y., "Collupulin" chill hazeproofing enzyme; Froberg type yeast.
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- (19E) Witteman Co., Inc., Elk and Selkirk Sts., Buffalo 5, N. Y.
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Food Yeast from Sulfite Liquor

Yeast Cream Is Dried on Twin Drums at Lake States Yeast Corp., Rhineland, Wis.

GORDON C. INSKEEP

Associate Editor

in collaboration with

A. J. WILEY, *Sulphite Pulp Manufacturers'*

Research League, Inc., Appleton, Wis.

J. M. HOLDERBY AND L. P. HUGHES

Lake States Yeast Corp., Rhineland, Wis.

THE disposition of spent liquors from the sulfite pulp industry has been the subject of a tremendous volume of research during the past 70 years. Pulp mills, individually and collectively, and research centers, public and private, have spent millions of dollars on the spent liquor problem.

In the broadest sense two general lines of approach have been used: (1) Treatment of the liquor to minimize the deoxygenating effect of its wood sugar content on receiving streams; and (2) utilization of the raw materials present in the spent liquor. Unfortunately, a completely satisfactory solution still remains to be found.

The original practice, which has been continued in most cases, was to discharge the spent liquor as produced, with no pretreatment, into the streams. Simple modifications of the principle of discharge to streams have been suggested and found applicable in a few situations.

Where very large bodies of dilution water are available some

mills have been able to build special discharge lines to achieve maximum dilution. This was done at Rayonier's Fernandina, Fla., plant, which pipes liquor 5 miles into the Gulf Stream, and at Camas, Wash., where spent liquor is distributed in the central currents of the large Columbia River. Another idea which may be feasible for some smaller mills involves storage of liquor in ponds and discharge during periods of high stream flow (1).

Although stream improvement has usually been and still remains the immediate objective of research efforts, increasing pressure from the laws of economics has emphasized the importance for concomitant utilization of this great amount of potential raw material.

Investigations into sulfite liquor treatment have resulted in processes utilizing the liquor itself or its components such as the lignin. Vanillin, oxalic acid, tanning material, road binders, dispersing agents in concrete, alcohol by fermentation, yeast by fermentation and others have been made from sulfite liquor.

Some of these processes have been successful commercially. The Monsanto Chemical Co. announced this spring that it is building a new plant on the West Coast for the production of vanillin from the lignin in the sulfite liquors. However, according to Hatch (4) it is theoretically possible to produce enough vanillin to satisfy the entire need of the United States from the spent liquor resulting from the production of 30 tons of sulfite wood pulp per day. Relatively few individual mills in the United States have a capacity below 100 tons per day. Obviously this is not the answer to the liquor disposal problem.

The same is true of the production of oxalic acid and a number of other by-products; these would provide an outlet for only a small portion of the spent liquor produced each year.

Spent sulfite liquor has been utilized as a source of calcium lignosulfonate for use with Portland cement either as a grinding aid or as an addition to the concrete mix to secure the benefits of cement dispersion (11). Here again the quantity of liquor thus far used is negligible in the industry-wide picture.

Another approach to the problem has been evaporation with subsequent incineration of the concentrated liquor as fuel. However, using the liquor from calcium-base pulping, a high percentage of steam so produced would be required for concentrating the spent liquor to burning consistency, and the economics of the over-all evaporation and burning operation have yet to be proved commercially in the United States.

With magnesium as the pulping base, liquor is produced which breaks down to magnesium oxide when incinerated under reducing conditions; the oxide can then be re-used in the pulp mill. This magnesia-base sulfite pulping process with the relatively new recycle aspects has recently been put into practice at the Longview, Wash., plant of the Weyerhaeuser Timber Co.

The fermentation approach has been used quite widely in Europe. Nearly all sulfite liquor in Germany is used to produce yeast or alcohol. However, European mills producing alcohol usually operate under a government subsidy not available to mills in this country. High operating charges and high plant investment discourage interest by any but the largest pulp mills in the United States. Furthermore, only the hexose sugars in the spent liquor are converted into alcohol by fermentation. These sugars account for 50% or less of the 5-day B.O.D., which means that this is a far from satisfactory stream improvement measure.

The fermentation of spent sulfite liquors to produce inactive dry yeast, although practiced by several plants in Europe, has been applied commercially in only one plant in the United States. This plant is operated by the Lake States Yeast Corp. at Rhineland, Wis. The technical problems are well under control and if the economic considerations can be sufficiently improved this will be one of the more promising solutions to the spent sulfite liquor problem in this country.

Briefly, the sulfite pulping process in general use today can be described as follows:

Sulfur is burned and the gases are absorbed in a lime suspension to form a solution of calcium bisulfite containing an excess of free sulfur dioxide. Other bases, such as sodium and ammonium as well as magnesium mentioned earlier, can be used to form the cooking acid.

Wood chips are cooked in the bisulfite at temperatures from 130° to 150° C. for 6 to 18 hours. During the digestion period lignin combines with sulfur dioxide or the sulfite ion to form soluble calcium lignosulfonate. After the cooking process is completed the acid liquor containing the dissolved materials is separated from the insoluble cellulose and is discharged as spent sulfite liquor.

Somewhat over 1 ton of dissolved wood solids for each ton of pulp produced is commonly present in this spent liquor. The organic material present in the liquor is complex; about 20% of the dissolved solids is made up of easily oxidized sugars and related products and 60% of more or less stable lignosulfonate

TABLE I. COMPOSITION OF SPENT SULFITE LIQUORS FROM SPRUCE WOOD

(Variations based on liquors of the same solids concentration)

	Grams per Liter	
Neutralized solids	...	100
Total sugar (as glucose)	...	15-22
Hexose	11-16	...
Pentoses	4-6	...
Volatile acids (as acetic)	...	2-5
Sulfur (all forms as SO ₂)	...	8-10
Total inorganic (free) SO ₂	0.5-2.5	...
Organic loosely combined SO ₂	3.0-5.0	...
Lignin (as lignosulfonate)	...	50-65
Calcium	...	7-10
Misc. compds.: solvents, aldehydes, uronic acids, resins	...	2-5
pH	1.5-3.0	

TABLE II. PRODUCTION OF SULFITE PULP IN THE UNITED STATES^a

Year	Tons
1940	2,607,789
1941	2,918,780
1942	2,930,272
1943	2,436,502
1944	2,386,149
1945	2,359,731
1946	2,476,468
1947	2,795,962
1948	2,811,216
1949	2,536,284
1950	2,855,825

^a Data are from the Census Bureau, U. S. Department of Commerce.

compounds. An average composition of spent sulfite liquors from spruce wood pulping is shown in Table I.

From an average size pulp mill (100 tons of pulp per day), some 20 tons of fermentable material are produced. When this amount is fed to the microbiological flora of streams, biological oxidizing processes are stimulated into roughly equivalent demands for some 20 tons of oxygen.

The annual domestic production of sulfite pulp in the 10-year period 1940-50 is shown by Table II. The production has averaged more than 2,500,000 tons per year. From this production there are some 500,000 tons of fermentable sugar wasted each year.

HISTORY OF YEAST PROCESS

Early recognition of the possibilities for growing *Torulopsis utilis* as a food and feed supplement material is credited to Delbruck and his coworkers at Berlin's Institute for the Fermentation Industry during the first World War. Fink, Lechner, and Just, working prior to and during World War II at the same research center, laid the laboratory and pilot plant groundwork for growing this organism commercially. Recognition of the pentose-consuming ability made possible the utilization of the hardwood liquors from the German pulp industry to give protein products capable of relieving critical food and feed shortages of the German Reich. Under stimulus and organization of the "Four Year Plan," the process reached the commercial stage with unusual speed.

Variations of the torula yeast process were developed more or less independently by several German pulp concerns. That of Zellstoffabrik Waldhof, involving unique aeration methods, was most successful, and the German industry, near the end of World War II, was asked to develop a standardized design based on that system for all new plants. Little, if anything, concerning German commercial methods, equipment, and know-how, was available on this method of yeast production outside Germany before the technical intelligence teams entered that country in 1945. Excellent reports were then prepared by Saeman, Locke, and Dickerman (9), Holderby (5), and others;

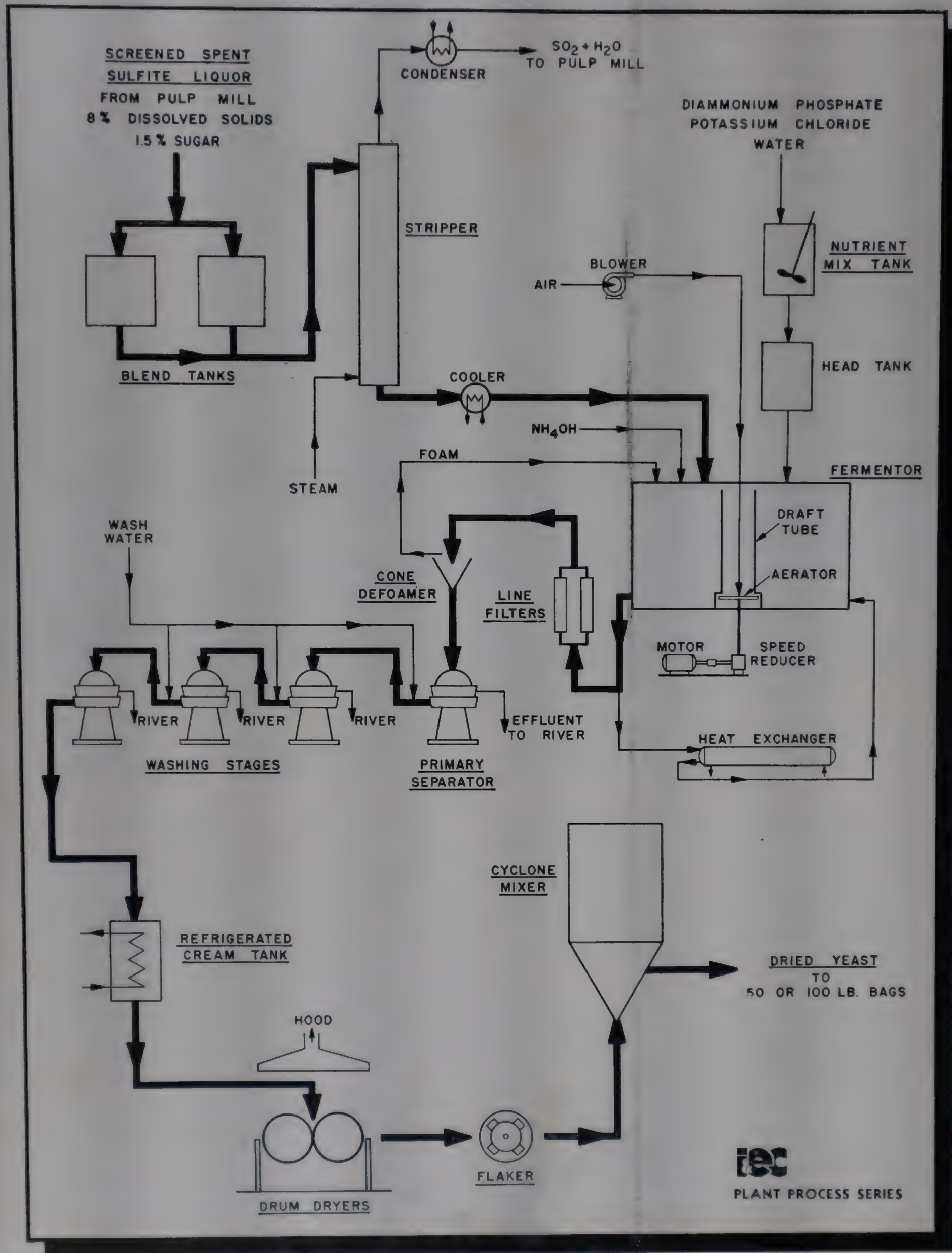


Figure 1. Flow Sheet for Production of Food Yeast from Sulfite Liquors at the Rhinelander, Wis., Plant of Lake States Yeast Corp.



Hot Spent Sulfite Liquors from Pulp Mill Are Stored in Wooden Blend Tanks

Tanks are constructed of fir staves, each has a capacity of 125,000 gallons

these have made the German versions of the process available generally.

A group of thirteen pulp mills in Wisconsin and Michigan, organized in 1939, and now known as the Sulphite Pulp Manufacturers' Research League, Inc., originally undertook study of the organism in this country. Microbiological processes capable of utilizing pentose sugars had not appeared feasible until then.

Active laboratory and pilot studies were initiated by this group in 1943, and a large pilot unit was built by the League in late 1944. All phases of the process were researched by the group for the purpose of developing new ideas and improving existing unit operations. Continuous operation of the pilot unit constructed at the Interlake Division of the Consolidated Water Power and Paper Co., Appleton, Wis., has been supplemented by engineering studies at various member mills.

Laboratory results were confirmed by the sustained pilot runs indicating the process could be expected to achieve 65 to 75% reduction in the biochemical oxygen demand of the spent sulfite liquor. In the meantime shortage of feed proteins, as a result of World War II, and newly developed demands for vitamin products offered definite promise of sufficient market value of the yeast product to justify the high capital investment and high operating charges. Without such returns the process could not have been expected to be practical as a waste treatment process; this concept still applies and serves as the chief limiting factor on wide scale application in the U. S. pulp industry at the present time.

The first commercial feed yeast plant to use spent sulfite liquor in the United States started production in 1948 with an initial design capacity of 4.5 tons of dry yeast daily. This was the Lake States Yeast plant at Rhinelander, Wis., which is described in this article.

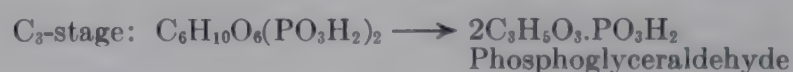
CHEMISTRY AND FERMENTATION MECHANISMS

Table I shows the approximate concentrations of sugars in waste liquors; actually the total solids in spent liquors range

from 60 to 150 grams per liter. The composition is subject to some variation due to the kind of wood used and the method and degree of cooking in the pulping process. Hardwood has a higher proportion of pentose sugar. The kinds of sugar are also a function of the wood used, and soft woods have been found to give a product of total sugar running about 70% hexose, largely mannose. Beech and poplar may have as much as 70% pentose sugars, largely in the form of xylose. A larger content of acetic acid is also found in liquors from hardwood pulping.

Mannose and xylose are both good carbon sources for the growth of *Torulopsis utilis*, but the xylose tends to be more difficult to attack and the yields are lower (more carbon dioxide and heat are given off). Hexose sugars are fermented more easily than the pentose sugars and may be selectively fermented in the presence of an abundance of both. The organism must be kept on a controlled feed to prevent an excess of hexoses building up, if the pentoses are to be fermented. Pentoses are not utilized in the alcoholic fermentation by *Saccharomyces* yeasts.

The complex reactions by which sugars, nitrogen, phosphorus, potassium, and minor trace elements are converted by yeast to new cell substance are not as well understood as those involved in the mechanism of alcoholic fermentation. However, according to Schmidt (10), the sugars first undergo a phosphorylation and splitting to three-carbon compounds and thereafter to two-carbon compounds, such as ethyl alcohol, acetic acid, and acetaldehyde:





Ingredients Are Charged Manually to Agitated Wooden Nutrient Mix Tank

These reactions are believed to be reversed for the synthesis of new carbohydrate cell material. The two-carbon compounds such as acetic acid, ethyl alcohol, and acetaldehyde are each suitable for complete yeast growth. Amino acids, fats, enzymes, and other carbon-containing cellular components are also capable of being synthesized from these original two-carbon compounds.

Nutritive Value of Torula Yeast

The yeast produced by the fermentation of spent sulfite liquors is a high protein and high vitamin product. An analysis of the torula yeast produced at the Lake States plant is shown in Table III.

Campbell and Ringrose (2, 7) have made extensive feeding tests on poultry using the torula yeast. It was their conclusion that the yeast could be used as a source of protein for growing chicks and laying pullets and that it was a good source of riboflavin and pantothenic acid. They found no differences in the nutritive value between torula yeast and brewers' yeast when fed in rations with or without animal protein.

Wiley, Dubey, Lueck, and Hughes (12) have reported chemical analyses and vitamin assays on samples of the dry torula-type yeast. In general, they found that samples produced commercially from sulfite liquor were uniform in chemical characteristics and in content of various components of the vitamin B complex.

The protein content of torula yeast constitutes about half its total weight, and the yeast compares favorably with milk and meat in amino acid composition. A typical amino acid assay of torula yeast is given in Table IV.

In a series of rat feeding tests at the Forest Products Laboratory, Harris, Hajny, and Johnson (3) compared the torula-type yeast with casein as a source of protein. When the rat diet was supplemented with methionine, they found that growth characteristics were comparable with those observed when the rats were fed the casein diet. However, without additional methionine, they reported that the gain in weight of the rats fed torula yeast was only 60% of that for the casein.

TABLE III. ANALYSIS OF TORULA YEAST PRODUCED COMMERCIALY FROM SPENT SULFITE LIQUOR

(All data on as-received basis)

	Chemical Analyses, %
Moisture, atmospheric drying, 2 hours at 105° C.	5.85
Ash	9.07
Phosphorus, as P	1.92
Calcium, as Ca	0.85
Crude protein (N × 6.25)	47.43
Crude fat	
Standard method	1.01
With prehydrolysis	4.84
Crude fiber, with HCl prehydrolysis	0.82
	Vitamin Assays, γ/Gram
Thiamine	5.3
Riboflavin	45.0
Pyridoxine hydrochloride	33.4
Pantothenic acid	37.2
Biotin	2.3
Niacin	417.3
Folic acid	21.5

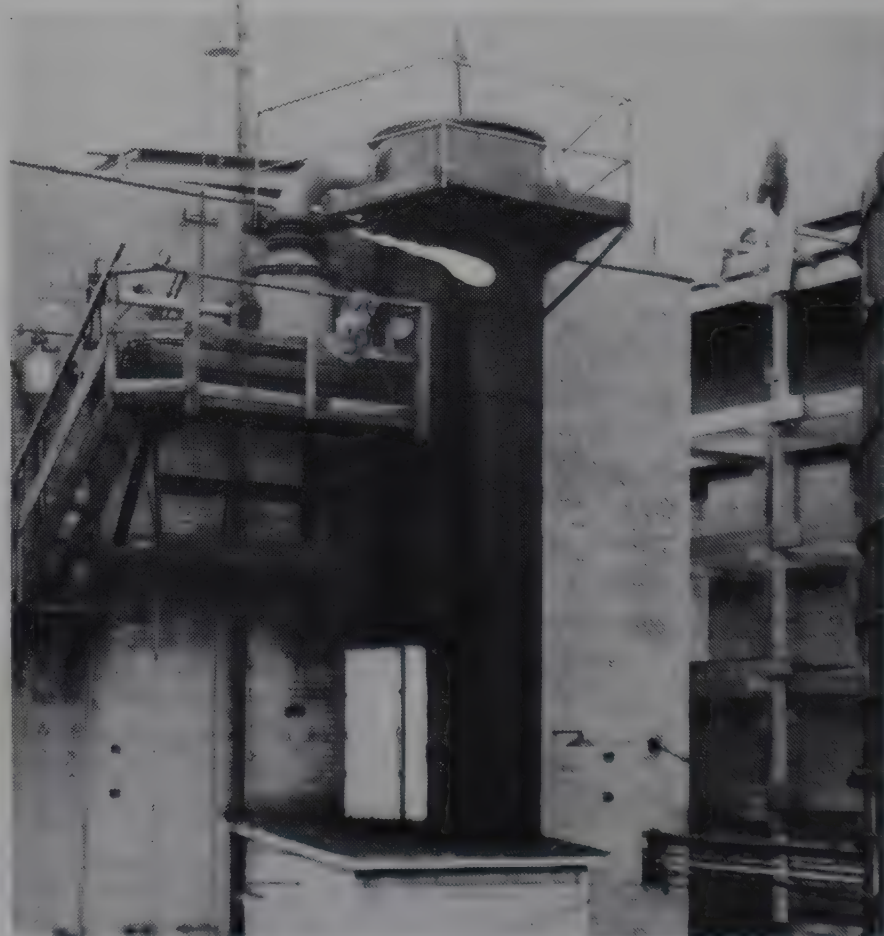
TABLE IV. TYPICAL AMINO ACID ASSAY OF TORULA YEAST^a

	% in Yeast ^a
Arginine	3.61
Cystine	0.68
Glycine	0.22
Histidine	1.31
Isoleucine	3.75
Leucine	3.57
Lysine	4.14
Methionine	0.84
Phenylalanine	2.41
Threonine	2.58
Tryptophane	0.66
Valine	2.98
Glutamic Acid	6.90

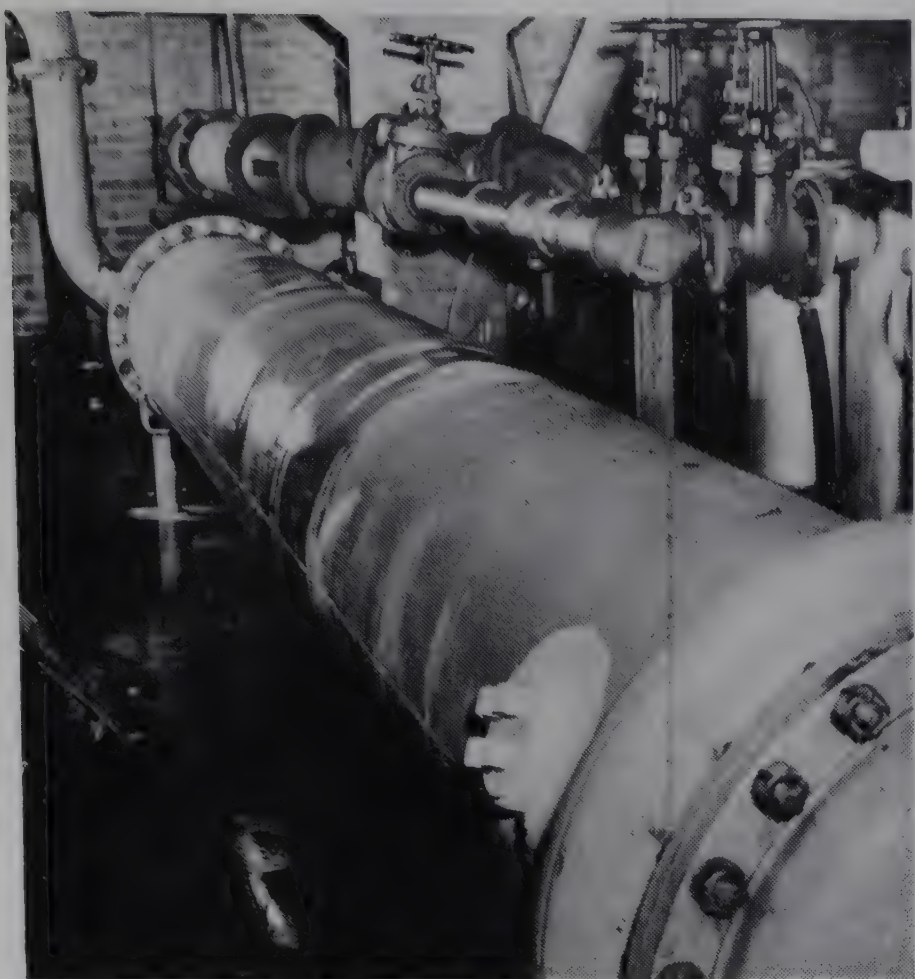
^a All results reported on basis of torula yeast as received.

At the present time the principal outlet of the torula yeast produced commercially by Lake States is to the feed supplement industry. Approximately 50 pounds of yeast per ton of feed is the normal recommendation for mixed poultry feeds.

The potential market for feed supplements is very large,



Sulfur Dioxide Is Removed from Feed Liquor by Steam Stripping in This Column



Shell-and-Tube Heat Exchanger for Cooling Fermenting Liquor

ranging into millions of tons annually; the exact figure depends to some extent on who does the estimating. The actual supplement market is growing with increasing knowledge of nutrition being gained on the research and practical levels, and even if the sulfite pulp industry could exploit its potential of 250,000 to 300,000 tons of yeast production annually, this would be only a small portion of the total demand. However, the competitive picture is very complex because of the many other products in the field in large volume.

Dry torula yeast has been accepted officially or tentatively as a wholesome food and feed material by regulatory organizations in this and other countries. Investigation is now being carried out at several universities with the object of further establishing the nutritive value of torula yeast as a human and animal food.

RHINELANDER, WIS., PLANT OF LAKE STATES YEAST CORP.

The new plant of the Lake States Yeast Corp. is situated adjacent to the sulfite mill of the Rhineland Paper Co. Waste sulfite liquor from the blow pits in the pulp mill passes through a 6-inch stainless steel pipeline on to a screen and thence into surge or blend tanks. The screen is 80-mesh stainless steel supported by a wooden frame. Corrosion was a problem at the Lake States plant. Materials of construction described in more detail later in this article were selected only after careful study.

Small amounts of wood pulp are retained on the screen and removed

manually at approximately daily intervals. The pulp is returned to the stock tanks in the mill for reprocessing. Figure 1 is a flow sheet for the Lake States process.

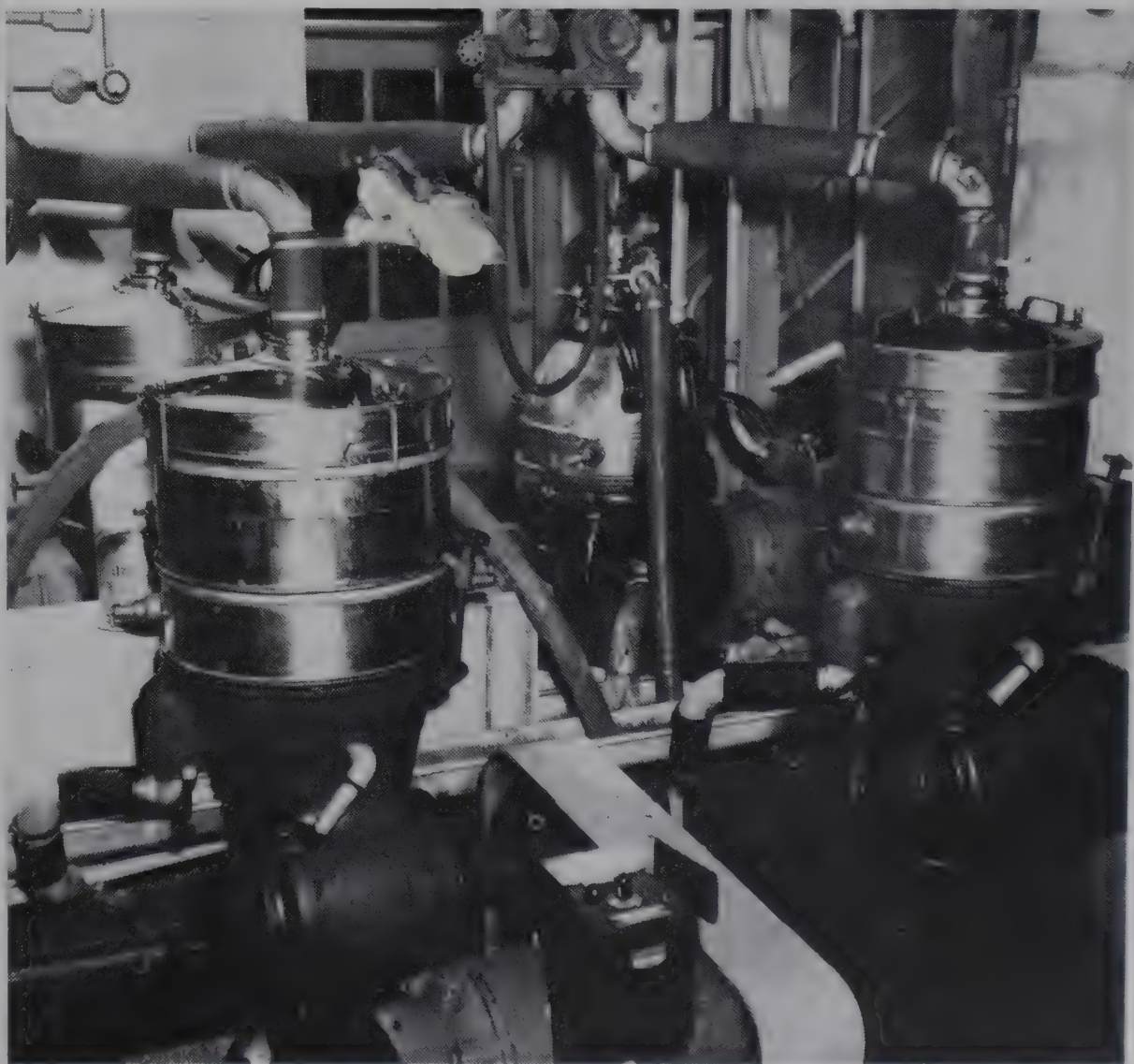
Preparation of Feed Liquor

Two blend tanks are provided, each with a capacity of 125,000 gallons. One is constructed of 6 × 6 inch and the other of 6 × 4 inch fir staves. Flow from the screen can be directed into either or both of the blend tanks. The tanks are 30 feet in diameter and 26 feet high and are not agitated. A surge capacity this large is important to the process in order to minimize the effect of changes in the composition of the liquor from the mill on the yeast fermentation.

The Rhineland Paper Co., as is the case with many pulp mills, produces several types of pulp from different woods, by different degrees of cooking, and by three different pulping processes (Mitscherlich, direct, and indirect quick cooks). The amount of sugar produced from hemlock and balsam woods is much less than that from spruce, and the liquors have different fermentation characteristics. The large storage and blending facilities serve to level off the sugar load in the feed liquor.

The spent sulfite liquor comes from the pulp mill intermittently at a rate of approximately 125,000 gallons per day. The fermentable sugar content of the liquor averages about 1.5% (approximately 80% hexose and 20% pentose), and the dissolved solids average approximately 8%. Temperature of the liquor is about 170° F., and the pH averages 2.5.

The hot sulfite liquor from the blend tanks is centrifugally pumped to a stripping still at a rate of 100 gallons per minute. The purpose of the stripper is to reduce the sulfur dioxide content of the liquor. The sulfur dioxide exists in a number of forms including total inorganic (sometimes called "free"), organic loosely combined, and firmly bound. The sulfur dioxide bound with lignin in the sulfone form is not of direct concern in the fermentation process and is not readily removed. The



Centrifugals Separate the Aqueous Solution and Yeast Cream

sulfur dioxide existing as sulfurous acid or simple salts of inorganic bases and that loosely bound with organics does inhibit yeast growth. German practice involved lime neutralization, but steam stripping has been found more suitable for the conditions at Rhineland.

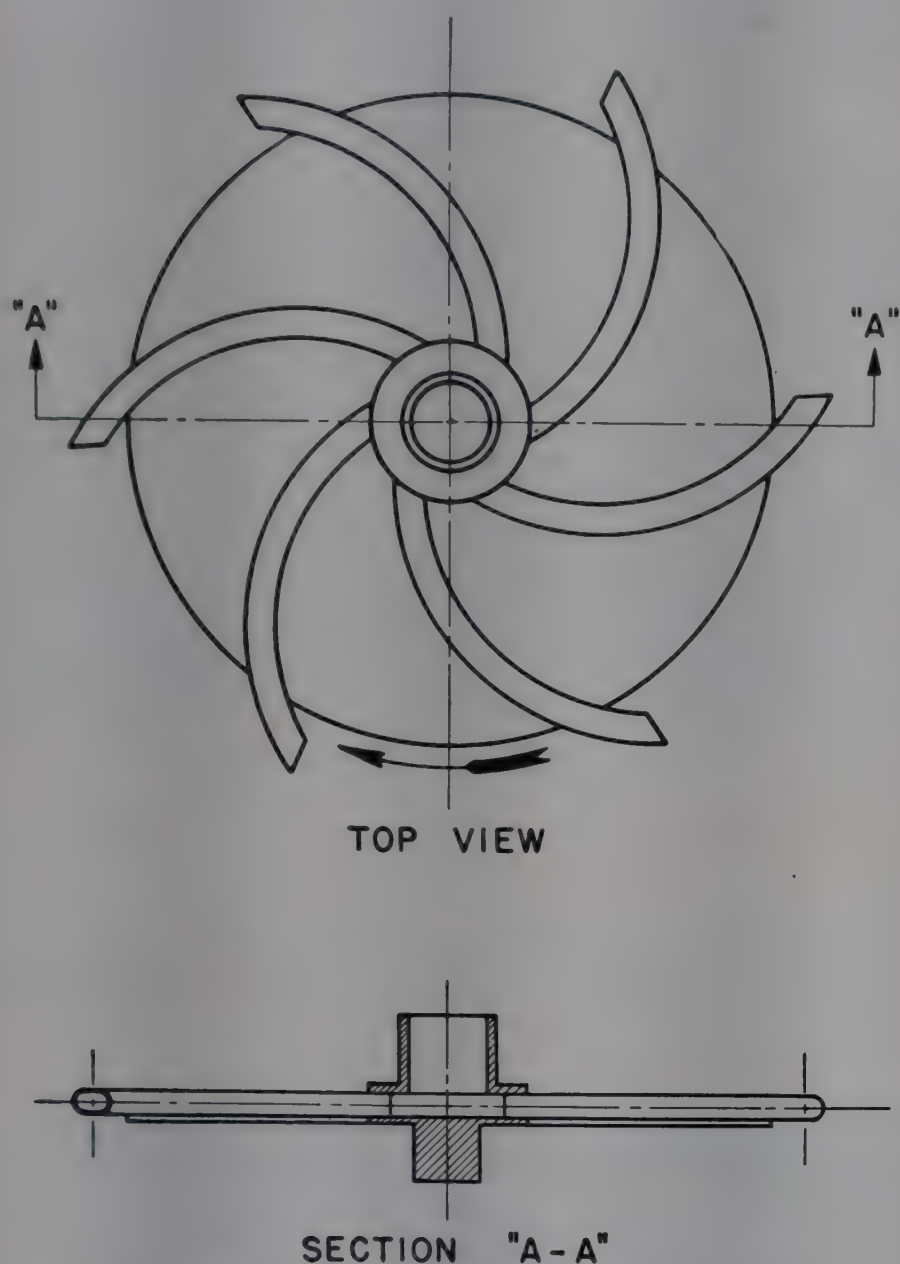


Figure 2. Principle of the Waldhof Aeration Wheel

Modification of this type aerator is used in the yeast fermentor at Lake States Yeast Corp.

The stripper is of stainless steel construction, 5 feet in diameter and 22 feet high. It is packed with Karbate (impervious carbon) 1 × 1 inch Raschig rings. The feed liquor comes in at the top, and live steam enters the bottom of the column through a sparge tube drilled with 22³/₈-inch diameter holes. The sulfur dioxide and water vapors pass through a stainless steel spiral-type surface condenser (1E), and the condensate is returned to the paper mill for re-use in the sulfite operation. The sulfur dioxide content of this condensate amounts to 8 to 10 grams per liter and represents an important sulfur conservation measure.

Fermentation

The stripped liquor leaves the bottom of the still column through an automatic level control valve (8E) at 180° F. and passes through a stainless steel spiral cooler (2E) entering the fermentor at approximately 80° F.

The fermentor is of carbon steel construction, clad with Type 304 stainless steel. It is an open-top vessel, 26 feet in diameter and 14 feet high, provided with a center draft tube 4 feet in diameter. The draft tube is supported by means of tie rods

attached to the fermentor walls. Operating volume of the fermentor is 45,000 gallons of emulsion (liquor plus entrained air) or some 20,000 gallons of liquor without air. This provides a holding time of approximately 4 hours in the fermentor.

Air is introduced into the fermentor through a rotating pin-wheel-like aerator composed of open-end tubes rotating at 300 r.p.m. The aerator is driven by a 250-hp. motor provided with hydraulic coupling and speed reducer and connected by means of a shaft through a packing gland on the bottom of the fermentor.

The aerator in use at Rhineland is a modification of the original German design used by Zellstoffabrik Waldhof. The German aeration system has been described in detail by Kiefer (6), and the wheel is illustrated in Figure 2. This general type of aerator design has also been incorporated in the pilot plant fermentor in use at Forest Products Laboratory. Saeman (8) has described this installation.

The air is supplied by a single-stage centrifugal blower (4E) having a capacity of 1700 cubic feet per minute; the blower is connected to the aerator by means of an 8-inch pipeline down through the center of the draft tube. It is not necessary to sterilize the air prior to use in the fermentation. The aerator serves not only as a means of supplying air but also as a liquor recirculation pump. The combination of this type aerator with the draft tube makes the addition of an antifoam agent unnecessary. The air flow is controlled manually by a butterfly valve on the suction side of the blower. The flow rate is measured by means of a standard orifice and water manometer tube set up. Once the fermentation is under way, only minor changes in the air flow are required.

Diammonium phosphate and potassium chloride are made up in a water solution in a 500-gallon wooden mix tank and pumped to a surge tank located above the fermentor. The mix tank is provided with a top-entering agitator (10E). Although the nutrient mixing is a batch process, the feed to the fermentor from the surge tanks is continuous and by gravity.

Anhydrous liquid ammonia is received by tank car and made into an aqueous solution to a concentration of approximately 20% ammonia. This ammonia solution is fed continuously to the fermentor at rates based on the sugar content of the feed liquor. The rate is manually controlled and indicated by a rotameter. The pH of the fermentation mixture (wort) runs about 5.0.

The stripped liquor, nutrients, and ammonia all enter the fermentor at or near the top of the draft tube. The flow through the tube is down, and this arrangement provides the most rapid mixing.

The temperature of the fermentation is controlled at 37° C. by circulating the wort through a shell-and-tube heat exchanger at the rate of 1500 gallons per minute. Using spruce spent sulfite liquor, 3750 calories of heat are evolved per gram of dry yeast produced. Liquors from hardwoods, high in pentose sugars, increase the cooling requirements. In Germany it was found that yeast production from beechwood liquor evolves 4600 calories per gram of dry yeast produced.

The wort is taken out of the bottom of the fermentor on one side and pumped to the bottom of the fermentor on the other side. Additional cooling, for use during the warm seasons, is provided by a water spray ring around the outside upper edge of the fermentor. The water is collected in a trough welded to the lower part of the fermentor.

The fermentation is continuous, and after an initial inoculation with the laboratory culture of *T. utilis* no further inoculations are required.

The yeast fermentation has been remarkably free from contamination. In more than 2 years of operation of the Lake States plant, production has never been interrupted because of contamination. The conditions of pH, temperature, and aeration with agitation permit the propagation of *T. utilis* at

rates rapid enough to overgrow and prevent the development of foreign organisms.

Yeast Separation

A side stream from the inlet to the fermentor heat exchanger is taken off at a rate equivalent to the total fermentor feed. This flow is manually controlled to maintain a constant level in the fermentor. The stream passes through two screen-type line filters (Figure 3) situated in parallel and then to a cone located above the open head of the fermentor. One of the filters can be taken off the line for cleaning without interruption of the operation.

The cone serves as a foam separator. Foam overflowing from the top of the cone is recovered in the fermentor. The liquor-yeast emulsion is taken from the bottom of the cone and flows by gravity to a centrifugal separator (7E). The aqueous solution is lighter than the yeast, and separation by centrifugation is relatively easy. The purpose of this primary separation is to get rid of as much of the liquor as possible. The relatively sugar-free separator effluent is discharged to the river.

The cream containing the yeast from the primary separator is collected in a cream trough and pumped to washing stage separators. Well water is used for washing and is pumped into the separator feed. The water layer from each washer is discharged to the river, and the cream is pumped to the following stage.

This washing operation is repeated in three stages. The effluent going to the river from the primary separator has an average fermentable sugar content of 0.2% compared with the 1.5% sugar in the fermentor feed liquor. The biochemical oxygen demand of the liquor processed is reduced approximately 65% by the operation.

The yeast concentration in the fermented wort to the centrifuges is about 1% on dry basis, and the primary stage concentrates amount to 10 to 12% solids. Subsequent washing steps give a cream to the dryer with 14 to 18% yeast solids.

Cream from the final washing stage is discharged to an agitated storage tank. This cream tank is insulated with 4-inch magnesia blocks and provided with coils connected to a conventional liquid ammonia refrigeration unit (11E); capacity of the tank is 1000 gallons. The cream tank is refrigerated only during periods when the fermentor is not in operation. If the fermentor is emptied, the cream tank is held under refrigeration and its contents are used as inoculum to start the fermentation again.

Drying

Yeast from the cream tank is pumped to twin drum rotary dryers (5E) of cast-iron construction. The drums, 42 inches in diameter and 120 inches long, are heated by steam under 80 pounds pressure. Vapors from the drying operation are collected by a hood over the drums and discharged to the atmosphere through a stack.

The dried yeast coming from the hot drums falls into a trough containing a screw conveyor (6E). It is then transferred by a bucket elevator to a flaker (6E). The flaker is a hammer mill type arrangement, consisting of a cylindrical screen with rotating internal blades.

The flaked yeast passes to a screw conveyor which discharges inside a cyclone mixer (3E). The mixer is similar in design to the conventional cyclone dust collector. The yeast is bagged from the cyclone mixer into 50- or 100-pound multiwalled paper bags. The product is nonviable and has an average moisture content of about 6%.

As with most industrial fermentations, operation is on a 24-hour basis, with shutdowns only in emergencies. The operating crews work in 6-hour shifts for a total work week of 36 hours. There are three operators on each shift, plus a small maintenance crew working only the day shifts. The control testing in the laboratory is done by the chief chemist.

CHEMICAL CONTROL

Depending on the complexity of the test or the need for immediate results, chemical analyses of the process samples are carried out by the nontechnical operating personnel, the plant chemist, or the research group of the Sulphite Pulp Manufacturers' Research League.

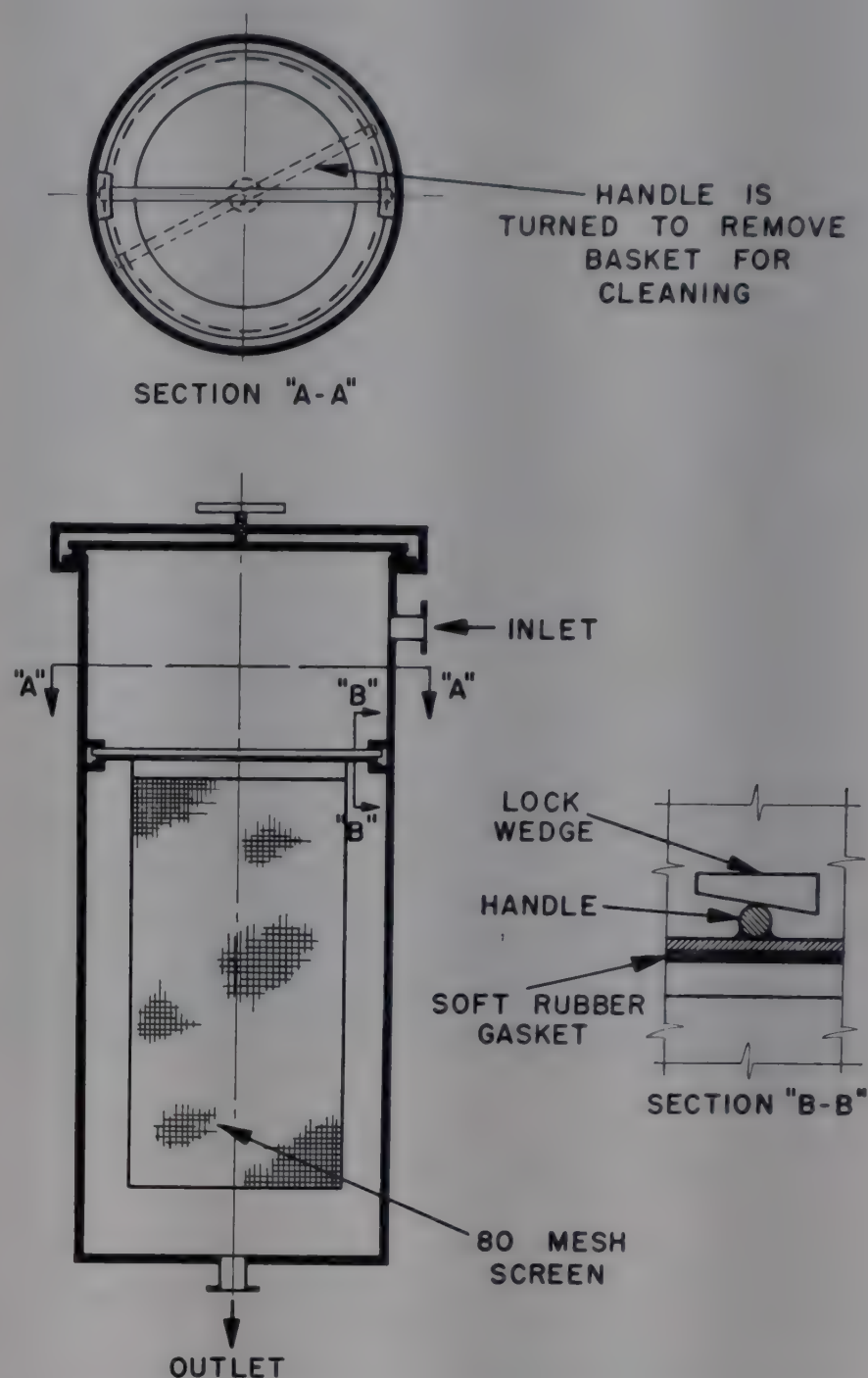


Figure 3. Cross Section of Line Filter Used to Clarify Feed to Yeast Separators

Filter was designed and built by Lake States Organization

The nutrient feed rates are regulated according to a quick sugar test run by the plant operators. Relative values for residual sugars are determined once each shift or oftener by rapid titration based on the Soxhlet method of sugar analysis. Results are available within a few minutes and serve as a quick guide for adjustment of the feed rates. However, because of the presence of variable amounts of other reducing substances, this test requires confirmation by at least daily checks using the more accurate but slower method in the chemical laboratory.

A simple centrifuge test for measurement of wet yeast volume in the fermentor is run under standardized conditions each hour. In this test a measured volume of defoamed wort is placed in Hopkins' vaccine centrifuge tubes and spun at 2000 r.p.m. for exactly 10 minutes. Under conditions of continuous yeast growth, this test provides a sensitive method of measuring the state of growth in the fermentor. Similar tests are run on



Research Work on Sulfur Dioxide Stripping

Small scale equipment is used by the staff of the Sulphite Pulp Manufacturers' Research League

samples from the separators as an indication of the efficiency of the yeast separating and washing steps.

In the chemical laboratory a complete sugar analysis is run each day as a check on the quick sugar test run by the operators. The more accurate method is based on use of a modification of the semimicro method of Somogyi on samples which have first been treated to remove lignin and other nonsugar reducing substances. In the chemical laboratory checks are also run each day on the Kjeldahl nitrogen analyses which are made twice each shift by the operators. Daily composites, based on hourly samples of raw, stripped feed, and centrifuge effluent liquors, are used for a check on the 5-day B.O.D. removal efficiency of the yeast plant.

The chemical laboratory determines moisture content by oven-drying on samples taken from each 1000-pound lot as produced. Periodic checks of phosphorus and ash content of the final product are also carried out using A.O.A.C. methods.

The Appleton laboratory of the Research League has taken care of the more complicated control tests for vitamins. Duplicates of all yeast samples and composites are forwarded there. However, at the present time a new spectrophotometer is being set up at the Rhinelander plant.

The spectrophotometer is primarily a research instrument to be used for developing colorimetric, turbidimetric, and fluorometric analyses in close cooperation with the Appleton laboratory which is already so equipped. Simpler control instruments

may be used eventually. Elemental analyses on the nutrients and substrates, new methods for turbidimetric control of yeast concentrations, and vitamin assays by various standard techniques may be made.

Practically all control tests for the yeast process were originally developed or adapted by the research staff, and this is also true of the vitamin assays and more complicated chemical testings. Table III indicates the chemical analyses and vitamin assays carried out on samples of the complex yeast product.

Samples are taken from every tenth 100-pound bag of yeast or twentieth 50-pound bag—that is, every 1000 pounds—in accordance with standard sampling techniques of the A.O.A.C. and the American Association of Feed Control Officials.

MATERIALS OF CONSTRUCTION

An extensive program of testing corrosion resisting alloys, coatings, and other construction materials led to adoption of Type 316 or 317 stainless alloys for all piping, pumps, and metal surfaces in contact with the raw feed liquor up to and including the stripper equipment. The stripped feed liquor, after removal of sulfur dioxide, can apparently be handled without difficulty by Types 302, 304, and 416 stainless alloys through the fermentor, emulsion cooler, and centrifuges. Baked-on Heresite phenolic-base coatings (9E) have been found excellent for yeast holding tanks in both the pilot and commercial units. For large liquor storage tanks, fairly good experience has been obtained with 4-inch thick Douglas fir heartwood tanks.

The fermentor in the Lake States plant is carbon steel clad with Type 304 stainless steel. In Germany, where cost and availability were prime factors, wood vats were found to be satisfactory. Newer fermentors in Germany have been constructed with concrete and lined with tile (9). Unlined concrete is undesirable because vigorous mechanical aeration and relatively low pH results in sand getting into the product.

The open fermentor with intense aeration leads to prevalence of high humidities on the operating floor. This has been a serious nuisance and causes an accelerated corrosion of piping and destruction of painted surfaces. Plans are currently under way to provide increased ventilating capacity. A similar problem in the dryer room was taken care of in the first year of operation by means of appropriately located ventilating ducts.

EFFLUENT

At the Lake States plant, samples of the feed and effluent liquors are taken each hour and are composited for B.O.D. analysis each 24-hour period. Average data for liquor processed in 1950 show 59.7% reduction in B.O.D. from all samples taken during the year. Monthly averages were improved with changes in processing methods, and a high of 64.5% was achieved during one month's run. Individual 24-hour composites frequently show 70% reduction of B.O.D. in liquor processed by the plant. Pilot plant data have demonstrated possibilities for 75% B.O.D. efficiency by the yeast process, and this serves as a goal for the commercial operation.

The remaining 25% of biochemical oxygen demand in the yeast plant effluent apparently results from carbohydrate material derived directly or indirectly from the hydrolytic breakdown of sugars. These products have yet to be fully identified. Numerous attempts to find means for practical biological processing have not been successful, but there is some possibility that this problem will also be solved.

Much speculation has attended the deoxygenating effect of the lignosulfonates present in spent sulfite liquor when disposed to streams and other dilution waters. Latest evidence points to the relative stability of these compounds. Appreciable degrees of lignosulfonate destruction apparently do not take place biologically in less than 20 days, and this slow rate probably does not show up in streams by present methods of measurement.



Dried Yeast from Cyclone Mixer Is Packaged in 50- or 100-Pound Bags

The Sulphite Pulp Manufacturers' Research League studied the effect on the B.O.D. of the effluent resulting from different degrees of treatment. This is a complex problem and variations are wide. A simplification of present conclusions and observations is summarized in Table V.

FUTURE

Research at the present time is directed toward improved aeration, better yeast recovery and washing, more efficient fermentor cooling, and further evaluation of the nutritive value of the yeast product.

The efficiency of aeration, agitation, and mixing in the fermentor are critical to over-all plant efficiency. Development work on this phase has been carried out by the Research League continuously since 1943 and substantial improvements are still believed possible. The power requirements of the method are high.

Much time was devoted to the study and development of the yeast separation and washing. Filtration by various methods,

both atmospheric and vacuum, and all types of centrifugal equipment have been investigated. These operations have been carried out both independently and in cooperation with the various equipment manufacturers. At the present time centrifugal equipment (12E) of German design is being studied with the hope that efficiency can be improved.

Cooling of the fermentor liquor with its large amount of entrained air is at its very best an inefficient process. As much of the heat as possible is removed from the feed liquor prior to entering the fermentor and the recovery of the heat for use in the pulp mill has been studied but as yet not applied in the present plant.

A number of research fellowships are being maintained at various universities in order that more information may be obtained on the nutritive value of the torula yeast. The yeast is apparently a quite satisfactory human food, and development of this outlet for the product might well change the entire economic picture of the process.

The future of the yeast from spent sulfite liquors seems to be dependent on the degree of success of cost reduction and product promotion efforts. It is now a question of economics more than of fundamental technology.

ACKNOWLEDGMENT

Portions of the introductory material for this paper have been derived from a chapter on Food and Feed Yeasts written by A. J. Wiley for publication in a new book, "Industrial Fermentations," L. A. Underkoffler, editor, Chemical Publishing Co. (in preparation).

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- (8E) Fisher Governor Co., Marshalltown, Iowa, level control valve, Type 410-50.
- (9E) Heresite and Chemical Co., Manitowoc, Wis., protective coatings.
- (10E) Mixing Equipment Co., Rochester, N. Y., Lightnin' mixer Model S-2.
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TABLE V. B.O.D. REMOVAL FROM SPRUCE WASTE LIQUORS^a
(Data are only approximate)

Extent of Treatment	Composition Change	Residual 5-day B.O.D., Mg./Liter	B.O.D., % Removed
None	Whole liquor	35,000	0
Pretreatment by stripping or precipitation	SO ₂ removed	31,500	10
Pretreatment and alcoholic fermentation	SO ₂ and hexose sugars removed	15,750	55
Pretreatment and torula yeast fermentation	SO ₂ , hexose and pentose sugars, and some acetic acid removed	8,750	75

^a 13% solids content (digester strength).



MODERN WINEMAKING

Oak and Redwood Casks and Tanks Are Used in Aging of Wine. Periodic Tests Are Made during Aging Period

WILLIAM Q. HULL

Associate Editor

in collaboration with

W. E. KITE AND RICHARD C. AUERBACH

Roma Wine Co., Fresno, Calif.

WINEMAKING has a long and convivial history. Since man first tilled the soil, the product of the fruit of the vine has been the consort of emperors and kings, the jovial companion of the poor as well as of the rich, and the ever popular theme of poetry, song, and story.

Just when man first discovered the grape to be the only fruit capable of naturally preserving itself, without anything being added to it or taken away, is not known. The first cultivated vineyards are lost in antiquity and there is no definite record of the beginning of wine. However, geologists have found evidence that grapes were a food of prehistoric man, and as the juice of pressed grapes turns naturally into wine, it is safe to assume that man drank this beverage before the dawn of history. The hieroglyphics of ancient Egypt and Babylon show the popularity of wine in that day, and records indicate that winemaking was practiced in China before 2000 B.C. (16). Approximately 165 Biblical references have added immeasurably to the colorful traditions associated with winemaking and to the use of wine as an important part of the customs of many ages.

As modern civilization was transplanted from the Near East into Europe, wine accompanied it. The Greeks were the first Europeans to cultivate vineyards and they taught the Romans. After Caesar's conquest of Gaul, Rome established wine growing as an important agricultural pursuit in Western Europe. Since that time, every country in Europe climatically suited to vine culture has made wine. Between 500 and 1400 A.D. Europe became the winemaking center of the world. Wine became the universal mealtime beverage and one of the staple necessities of life in European wine-consuming countries. Many volumes have been written picturing old world wines and winemaking (1, 4, 5). This article describes modern winemaking in the western part of the United States.

The Franciscan fathers brought grape cuttings and seeds with them from Mexico when they settled in California in the late eighteenth and early nineteenth centuries. Vineyards were established at the early missions and, in fact, the fathers were the only wine growers in the state until 1824. While their wines were chiefly for religious services, table and medicinal use, and hospitable entertainment of visiting travelers, some was sold in small lots and the quality of California wines became well known.

At the present time, wine is commercially made in 29 of the 48 states. In 1949-50, total net production exceeded 100,000,000 gallons (Table I). California produces approximately 90% of the nation's total in three to four hundred wineries with capacities ranging from 10,000 to almost 20,000,000 gallons per year. New York's production ranks second. California's wineries produced 125,000,000 gallons of wine in the 1950-51 season, an increase of 25% over the year preceding and the third largest output on record. During the years of prohibition, more wine was made than before the passing of the 18th Amendment (10). However, most of it was made in cellars of residences in large cities for family use and was generally of very poor quality.

Of great importance is the difference in the product of California and the balance of the winemaking states. With few exceptions, California, because of its mild climate and suitable soil, was early found to be the only state where the *Vitis vinifera* or European family of grapes can be successfully grown. The state's wine, raisin, and table grapes are members of the European family. Most other American wines are from the *Vitis labrusca* species, which are characterized by their so-called foxy flavor and aroma. The Catawba and Concord grapes are examples of the latter. The wines of these grapes are distinctly different from those of European grapes, with spicy flavors and aromas entirely their own.

TRADE GLOSSARY

Acidity	In wine, acidity is the word normally used to indicate the quality of tartness or sharpness to the taste, the presence of agreeable fruit acids, an important favorable element in wine quality. Not to be confused with sourness, dryness, or astringency.	Dessert wine	Sweet or partially sweet still wines containing approximately 20% alcohol by volume and to which a proportion of brandy has been added to arrest fermentation, leaving a portion of the original grape sugar unfermented.
Appetizer wine	Wines of dessert wine class which are usually served before a meal; includes sherry and vermouth.	Dry	A term indicating that all grape sugar in a wine has been fermented to alcohol.
Aroma	That part of the fragrance of wine which originates from the grapes used; as distinguished from "bouquet."	Fruity	Having the fragrance and flavor of the grape; sometimes used to designate a combination of tartness and sweetness; "grapy."
Balling or Brix	A measure of density in degrees which indicates total solids, primarily sugar content, of grape juice; on wine it is the relative sweetness.	Generic	Wine names based on definite type characteristics, such as sauterne, Burgundy, and sherry.
Body	Consistency, thickness, or substance of wine as opposed to lack of body in thin wine; reflects the quantity of solid matter or extract in solution in the liquid.	Lees	Sediment deposited by wine during storage on aging.
Bouquet	That part of fragrance of wine which originates from the fermentation and aging as distinguished from "aroma," the fragrance of the grape.	Must	Unfermented grape juice, with or without the substance of the crushed grapes.
Brandy	A spirit distilled from wine; beverage brandies are 100° or below in proof; neutral brandies are of 170° to 189° proof	Nutty	English term denoting the characteristic pungent flavor of sherry, which the Spanish call "rancio."
Cooperage	Bulk wine containers ranging in size from barrels to large tanks.	Pomace	The pulp, skins, and seeds of grapes remaining after the juice of newly fermented wine has been drawn or pressed out.
Cuvee	Literally, the contents of a cask of wine, but usually refers to an especially prepared blend of wines, such as a blend of still wines before secondary fermentation to produce champagne.	Racking	The drawing of wine off its lees or the transfer of wine from one tank to another.
		Table wine	Wines containing not over 14% alcohol by volume; usually consumed with a meal.
		Varietal	Wine named from principal grape variety from which it is made is said to have a varietal name. It must contain 51% or more of that grape, such as muscatel and Zinfandel.

WINE CHEMISTRY AND TYPES OF WINE

Wine is the product of the partial or complete fermentation of the juice of sound, ripe grapes. Although various wine experts and interested governmental agencies have defined it in slightly different terms for various and special reasons, all agree that wine is essentially a fermented alcoholic grape beverage. By law, if made from a fruit other than the grape, the wine must be identified as to its fruit source. Furthermore, by California law California grape wine may be made only from grapes grown in California and the addition of sugar is prohibited.

Crushed grapes and their juice, commonly referred to as "must," contain sugar, organic acids, tannin, flavoring substances, proteins, mineral salts and pectin, various mucilaginous materials, and many other trace substances. Yeasts, bacteria, and fungi,

some desirable and others undesirable, are also present. Table III lists the ranges in composition. Wine is the result of the changes which these substances undergo during fermentation and after processing.

Organic acids, particularly tartaric, assist in producing sound and healthy wine. Desired range is between 4 and 8 parts per thousand, depending on the type of wine. This concentration ensures a full-tasting wine which stores well, whereas too little acid results in a flat taste and short life. In most countries, it is permissible to correct an acid deficiency through the addition of fruit acids such as citric, malic, or tartaric. Acids also ensure a better extraction of color, but if present in excessive amounts render the wine too tart.

Tannin is an essential component of the wine and is extracted from the skins and seeds of the grape. It aids in the clarification of wine and produces a more brilliant color. An excess gives astringency which delays the final aging of the wine.

During the aging of wine, the flavoring substances undergo many changes and to a great extent control the flavor of the end product. The exact nature of many of these changes is not fully known and much current research is being directed in this field.

In fermentation, the natural grape sugar is transformed by action of wine yeast into carbon dioxide gas and wine alcohol summarized by the reaction:



Dextrose or levulose Ethyl alcohol Carbon dioxide

The transformation is not as simple as indicated by this equation, however, for several intermediate reactions are involved. The quantity of alcohol and carbon dioxide formed and the kind and concentration of by-products vary with the strain of yeast and fermentation conditions. Amerine (2) has reported the work of other investigators who used champagne wine yeast to obtain as actual products of fermentation the compounds tabulated below. These are compared with the theoretical products. It is not implied that these are the only products of fermentation.



Efficiency of Filtration Tested by Observing Clarity of Wine with a Pulfrich Photometer with Turbidimeter Attachment

MODERN WINE MAKING

ibc
PLANT PROCESS SERIES

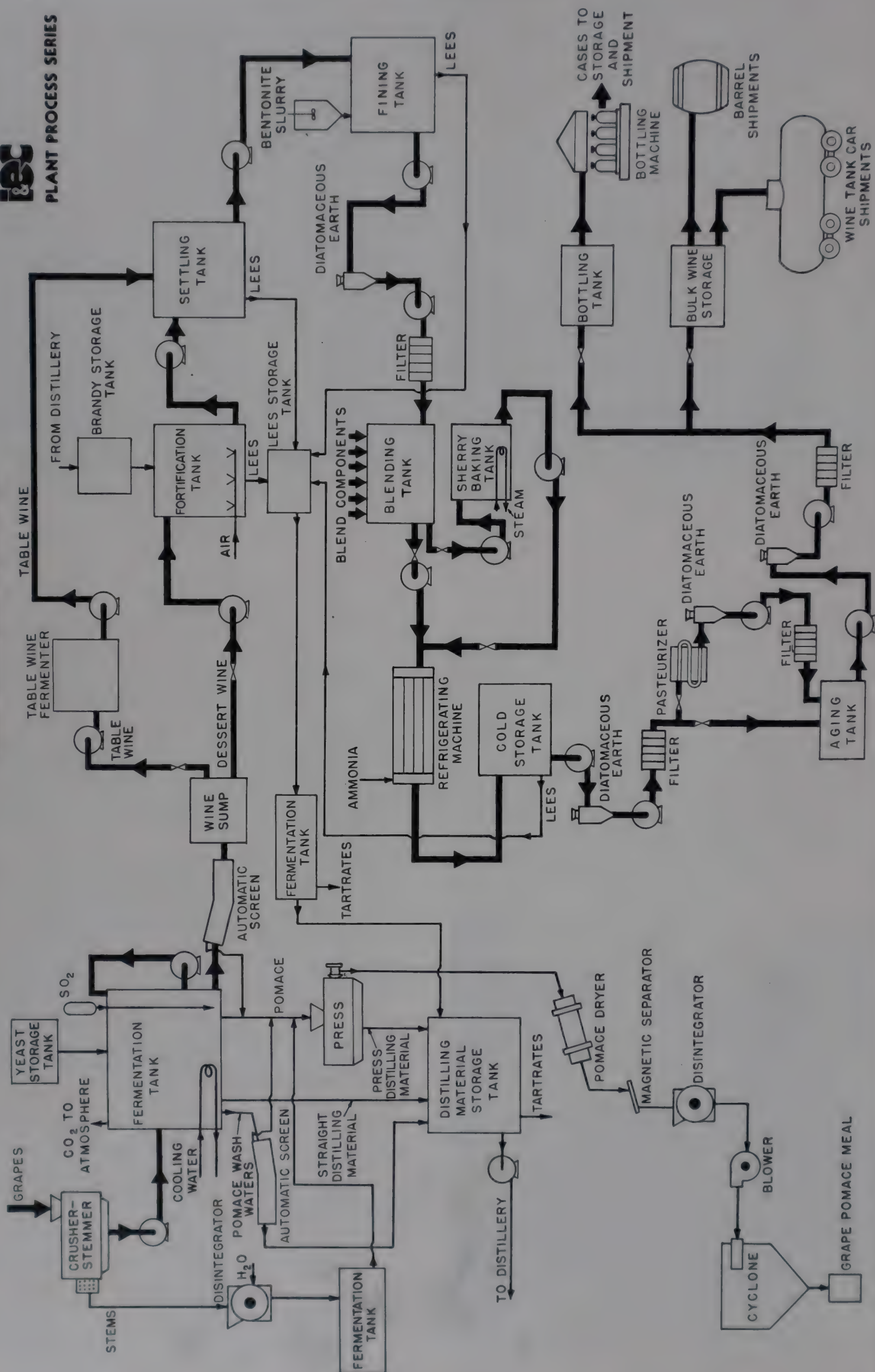


TABLE I. CALCULATED NET PRODUCTION OF U. S. WINE (18)

(Thousands of gallons)

Year Ending June 30	Table Wine		Dessert Wine		Vermouth		Sparkling Wine		Total		Grand Total
	Calif- ornia	Other states	Calif- ornia	Other states	Calif- ornia	Other states	Calif- ornia	Other states	Calif- ornia	Other states	
1936-40 ^a	16,528	5,507	47,380	2,252	72	130	95	319	64,075	8,208	72,283
1941-45 ^a	23,733	10,905	59,981	2,747	1,057	1,249	377	818	85,148	15,719	100,867
1946	22,374	6,282	81,169	589	1,386	1,420	666	1,294	105,595	9,585	115,180
1947	30,141	7,435	121,377	2,750	847	1,160	938	1,432	153,303	12,777	166,080
1948	17,516	5,182	77,006	981	498	1,287	202	767	95,222	8,217	103,439
1949	22,612	5,361	107,318	1,092	616	1,753	396	697	130,942	8,903	139,845
1950	17,093	7,252	74,092	1,082	719	1,733	423	589	92,327	10,656	102,983

^a Average.TABLE II. TOTAL APPARENT CONSUMPTION^a OF COMMERCIALY PRODUCED WINE IN UNITED STATES (18)

(Thousands of gallons)

Year	United States					Foreign Wine					Grand Total
	Table	Dessert	Vermouth	Sparkling	Total	Table	Dessert	Vermouth	Sparkling	Total	
1936-40 Av.	22,130	45,605	265	410	68,410	1,900	..	1,265	513	3,667	72,078
1941	28,719	68,779	1,400	918	99,816	301	629	621	104	1,629	101,445
1942	31,763	77,706	1,722	845	112,035	123	437	365	98	1,003	113,038
1943	37,391	52,241	2,587	1,206	93,025	305	3,168	528	84	4,075	97,501
1944	35,703	51,037	2,741	1,395	90,876	446	6,761	791	87	8,079	98,555
1945	27,254	60,420	2,215	1,418	91,309	231	1,735	590	149	2,667	93,975
1946	36,472	93,864	3,045	2,055	135,436	941	2,370	1,159	546	4,880	140,316
1947	22,605	69,357	1,422	1,010	94,393	535	689	862	182	2,267	96,660
1948	27,594	88,621	2,112	1,063	119,389	889	658	979	375	2,901	122,290
1949	30,900	95,042	2,385	1,045	129,373	1,158	584	1,021	431	3,195	132,567
1950	33,871	97,861	2,769	1,121	135,622	1,882	708	1,484	593	4,667	140,289

^a Apparent consumptions based on tax-paid withdrawals, tax stamp sales, shipments received for consumption, sales by wholesalers to retailers, and sales by state stores to consumers and others. Actual consumption figures are not ascertainable from any statistical source.

Product	% of Fermentable Sugar Transformed	
	Theoretical	Actual
Alcohol	51.1	47.8
Carbon dioxide	48.9	47.0
Acetaldehyde	0.0	0.01
Acetic acid	0.0	0.61
2,3-Butylene glycol	0.0	0.06
Glycerol	0.0	2.99
Lactic acid	0.0	0.40
Succinic acid	0.0	0.020-0.045

The yield of alcohol by weight is generally 47% in contrast to the 51.1% theoretically possible; the remainder of the sugar is converted into other products and materials that are used by the yeast for growth and respiration.

While there are literally hundreds of different names by which wines are known, some generic and some varietal, the classification of wines need not be complex or confusing. They are generally classed according to use; however, in a broad sense, all wines may be considered as either still wines or sparkling wines. The still wines include table and dessert wines. Table wines are further divided into red and white wines based on their color, and dessert wines are subdivided into sweet wines (red, amber, and white) and appetizer wines. Sparkling wines are principally white and pink champagne and red sparkling Burgundy. Popular names most frequently applied to California wines are shown in Table IV.

Winemaking can be briefly summarized. Picked grapes are transported to the winery, where they are crushed and the stems separated from the skins, fruit pulp, and seeds by a combination crusher-stemmer. Crushed grapes and juice are pumped to either open or closed fermenting tanks where sulfur dioxide in small quantities is added to inhibit the growth of wild yeast and undesirable bacteria. Pure wine yeast is then added and fermentation soon thereafter begins. At desired degree of fermentation, fermented juice is racked either to storage or to fortifying tanks and pomace is conveyed to presses for removal of liquid and by-product manufacture.

After clarification, filtering, blending, and aging under controlled conditions, the exact treatment varying with kind of wine being made, wine is ready for bottling and storage or shipping.

ROMA WINE CO. AT FRESNO, CALIF.

Wine was first made at the site of what is now the Roma Wine Co.'s Fresno, Calif., winery in 1933. The property at that time

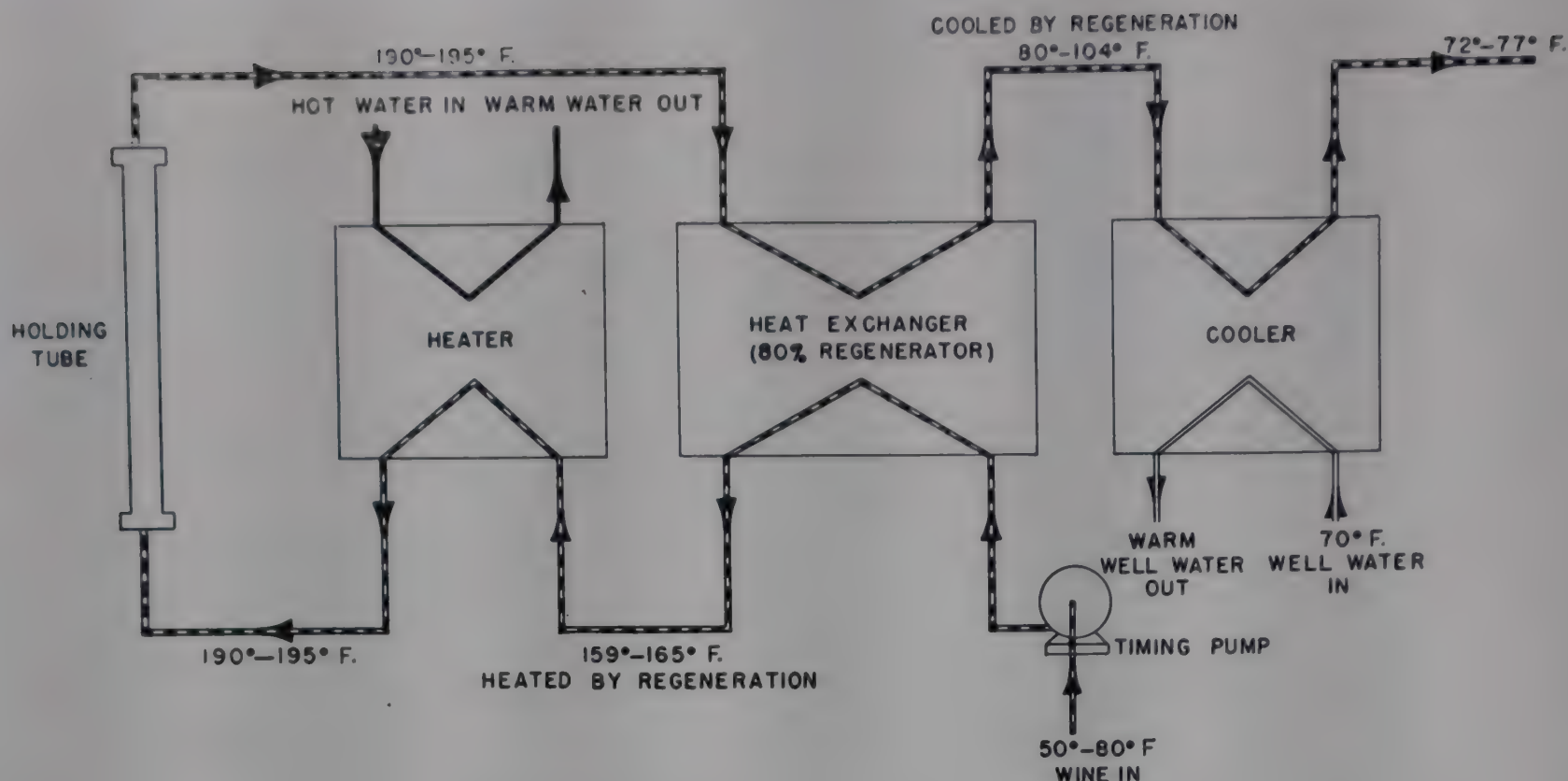
was owned by Santa Lucia Winery, Inc., and the operation was very modest in size. In 1935, the winery was purchased by the Roma Wine Co., owned and operated by John B. Cella and Lorenzo Cella, who had immigrated from Italy at the turn of the century and had earlier bought a winery at Lodi, Calif. During the first season of their operation at Fresno, over 20,000 tons of grapes were crushed. Expansion after expansion followed at Fresno until, by 1941, the winery had become known as one of the world's largest and most modern with facilities for crushing over 2000 tons of grapes daily. Roma Wine Co. was acquired by Schenley Industries, Inc., in 1942. Roma now has wineries in Kingsburg and Lodi, Calif., in addition to the one at Fresno.

The winery at Fresno today has a crushing capacity of 80,000 tons of grapes a season, which generally runs from the latter part of August or first of September to the end of the year. Total wine storage capacity is over 15,000,000 gallons. Winery buildings and operating areas cover 55 acres. An experimental vineyard has rows of over 70 grape varieties and includes almost all varieties commercially grown in California.

Grapes used by Fresno are grown in the San Joaquin Valley within a radius of 60 miles of the winery. All are of the *Vitis vinifera* family. White grapes represent 70% of the total grapes

TABLE III. RANGES IN COMPOSITION OF GRAPE MUST (6)

Constituent	Range, %	Comments
Water	70-85	
Extract	15-30	Sugar-free about 1.5-3.00
Carbohydrates, total	12.2-28.5	Invert sugar in vinifera grapes
Sugars	12-27	
Pectins	0.1-1.0	Includes gums
Pentosans	0.1-0.5	Also small amounts of pentoses
Inositol	Traces	
Acids, total	0.3-1.3	pH ranges 2.9-3.9
Malic	0.1-0.5	
Tartaric	0.2-0.8	Much is K bitartrate
Citric	Traces	
Tannin	0-0.20	
Nitrogen	0.1-2.0	(0.0625-1.30 as protein)
Ash	0.2-0.6	
ASH CONSTITUENTS		
Iron	0.0001-0.0030	Chiefly from dust or iron equipment
Potassium	0.040-0.2000	Varies with maturity, etc.
Calcium	0.0040-0.0150	Increases in concrete tanks
Magnesium	0.0050-0.0200	
Aluminum	0.0001-0.0040	Some filter aids increase this
Sodium	0.0050-0.0200	
Manganese	0.000-0.0050	



Wine Pasteurization in Regenerative Unit

Sections may be used individually for other winery purposes. As an example, the heating section may be used as a sherry cooker or as a heater prior to bottling. The cooling section may be used to cool dry wine for cellar storage at 60° to 65°. The regenerating section may be used in the process of chilling wine.

crushed and include chiefly Muscat of Alexandria, Fehér Szagos, Palominos, Malagas, and Thompson Seedless, the last two being used principally for brandy and grape concentrates. The principal black grapes used are Zinfandel, Petite Sirah, Mission, Grenache, Carignane, and Salvador. Over 95% of the grapes used are bought from the individual growers on both contract and door purchases. (They may be purchased on the basis of their sugar content or by straight tonnage.) Grape prices fluctuate considerably during the season and are posted daily.

CRUSHING

Roma's winery is a scene of much activity during the crushing season. Grapes are brought to the winery in 20-ton side-dump trucks and trailers and lined up in lanes by variety. The grapes

are first inspected by the representative of the county department of agriculture, who is the official sugar tester. Four samples are taken from each 20-ton load. The variety of grapes is verified, a visual observation of the quality is made, and the sugar content of the juice is determined, from which the alcohol content of the fermented product may be predicted. The sugar test, made by means of a Brix or Balling hydrometer, gives the concentration of a sucrose solution of the same density as the juice being tested. The degrees Brix or Balling are approximately double the percentage of alcohol by volume that will result by normal fermentation. Sugar testing techniques as well as many other wine-testing procedures have been described in detail (11). Grapes for table wines are generally picked at a time when their juice tests 20 to 25 degrees Balling and for dessert wines when the juice is 22 to 26 degrees Balling. After acceptance, grapes are weighed on a 60 by 10 foot motor truck scale which handles a 20-ton truck and trailer simultaneously (11E). The driver then waits his turn at the crusher, the crushing schedule being planned by the fermenting room supervisor.

There are two types of crushers used in California wineries, the roller and the Italian type. The latter is more common today (?).

In the roller type, grapes are crushed between two fluted horizontal rolls of bronze or stainless steel which turn toward each other. Adjustment in the rolls allows grapes to be thoroughly crushed without breaking the seeds or grinding the stems. Crushed grapes and stems pass through the rolls into the stemmer, which consists of a stationary perforated horizontal cylinder through which the grapes fall and out the end of which the stems are kicked by rapidly revolving metal paddles.

Roma uses a nonroller-type crusher stemmer. Trucks move from the scales to the crusher bins, which are concrete and are approximately 100 feet long and 2 feet wide at the bottom, increasing to 5 feet in width at the top. Most growers use side-dump tank trucks which are emptied by a truck crane which tilts the truck and allows the grapes to spill into the bin. A continuous bronze drag chain conveyor with wood cleats carries the grapes along the concrete bin to the crusher. A truck and trailer with a load of 20 tons of grapes is normally emptied in about 10 minutes. Microcrystalline wax has been found to be the best coating for the concrete bins as well as the walls of concrete fermenting and storage tanks (15), although many other materials have been investigated (12). As the grapes move toward the crusher, they pass over a stainless steel, Type 304, screen with $\frac{1}{8}$ -inch perforations. Free-run juice passes through the screen to a concrete sump where it is added to the discharged must from the crusher.



Yeast Propagation from Agar Slant to Plant Size Starters, a Stepwise Procedure

There are four crushers at Roma's winery. The two more commonly used are heavy-duty rotary crushers which achieve high efficiency in crushing and stemming by centrifugal action (13E). Grapes are fed into a 30 by 42 inch mild steel hopper and enter a horizontal perforated cylinder, 30 inches in diameter and 10 feet long, and made of low carbon steel. It contains 0.5 by 1.5 inch slots in the feed end and 1.5-inch perforations in the discharge end. The screen revolves at 24 r.p.m. Revolving paddles inside the cylinder rotate at 500 r.p.m., remove the stems from the grapes, and force the grapes through the perforations. The combined effects of the two moving parts thoroughly crush the grapes, and the must passes through perforations in the cylinder to a sump below. An extra heavy-duty semidisplacement-type centrifugal pump, made of cast bronze with a manganese bronze impeller, and operated by a 40-hp. 1800 r.p.m. motor with a multiple V-belt drive, takes the must from the sump to the fermenting room through a 6-inch copper line. Capacity of the pump is from 100 to 185 tons of crushed grapes per hour (14E).

Grape stems contain 7 to 8% sugar. They were formerly a waste product and the sugar was not recovered. The Roma winery at Fresno pioneered in developing a process whereby the sugar from the stems is recovered and fermented.

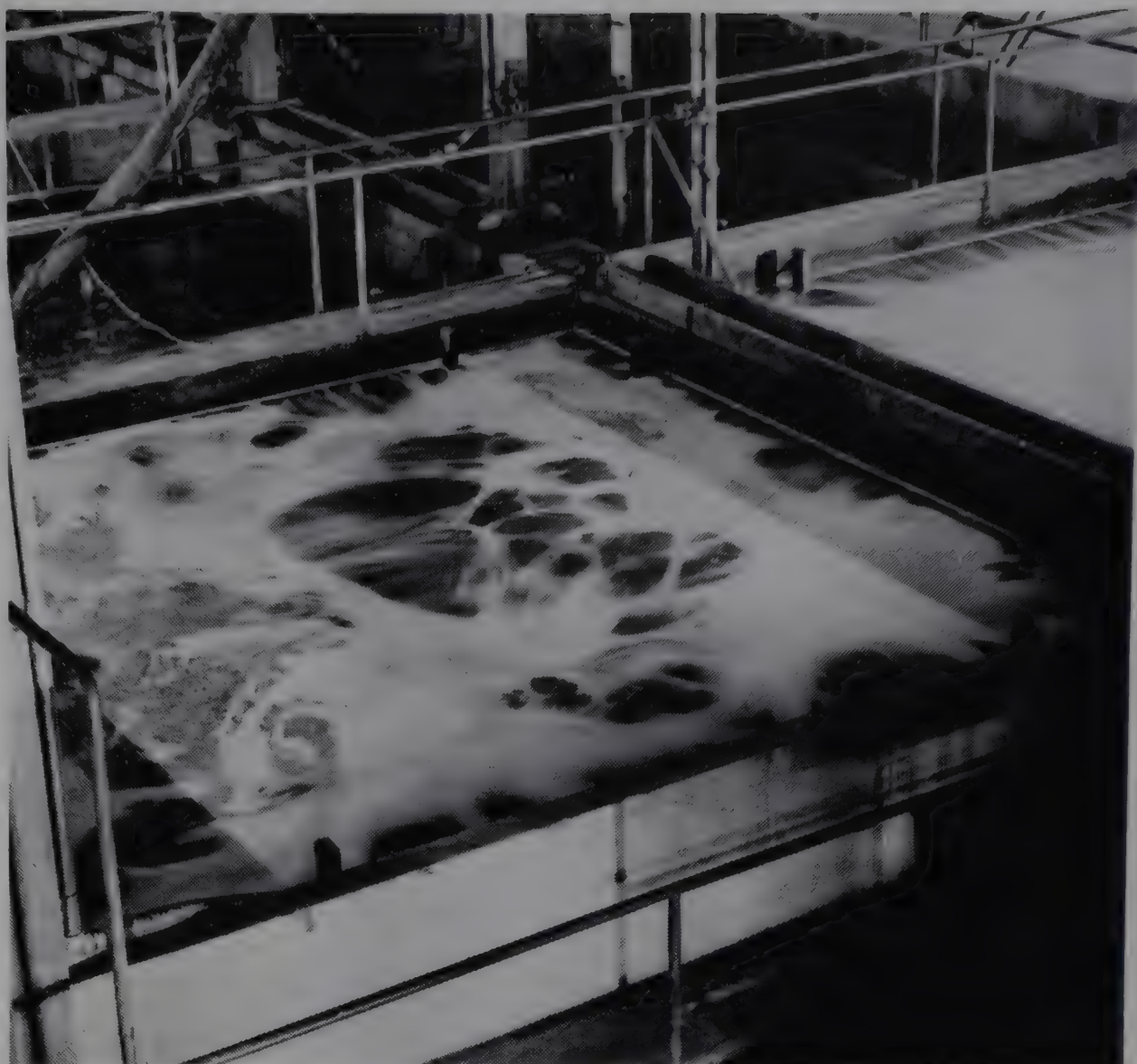
Stems are thrown from the combination crusher-stemmer onto a belt conveyor, which takes them to a pulp disintegrator of the type and size normally used in the wood pulp industry (6E). The disintegrator is equipped with a pre-breaker feeder that disengages the stem bunches. Stems are then shredded and hydrated. The slurry discharge, 4 to 6% in consistency, is used only as distilling material for neutral grape brandy.

FERMENTATION

The natural grape sugar is converted into potable alcohol and carbon dioxide by action of enzymes provided by true wine yeast,

TABLE IV. CALIFORNIA WINE TYPES

STILL WINES			
Table wines			
Red			
Claret	Cabernet	Grignolino	Zinfandel
Burgundy	Carignane	Petite Sirah	
Barbera	Charbono	Pinot Noir	
Barberone	Chianti	Pinot Red	
Aleatico	Gamay	Rose	
White			
Rhine	Folle Blanche	Moselle	
Sauterne	Golden Chasselas	Pinot Blanc	
Dry sauterne	Gutedel	Riesling	
Sweet sauterne	Hock	Sauvignon Blanc	
Haut sauterne	Light Muscat	Semillon	
Chateau sauterne	Malvasia Bianca	Sylvaner	
Chablis	Moscato Canelli	Traminer	
Chardonnay	Muscat Frontignan	Ugni Blanc	
		White Chianti	
Dessert wines			
Sweet			
Port	White port	Muscat Frontignan	
Muscatel	Angelica	Red muscatel	
Tokay	Malaga	Sweet sherry	
Appetizer			
Sherry	Madeira		
Pale dry sherry	Marsala		
Vermouth			
SPARKLING WINES			
Champagne		Sparkling sauterne	
Sparkling Burgundy		Sparkling Muscat	
Pink champagne		Moscato Spumante	
		Sparkling Moscato	



Open Concrete Tanks Where Red Wines Are Fermented

Saccharomyces ellipsoideus. This yeast is found on the skins and stems of grapes, and it was formerly common practice to allow crushed grapes or their juice to ferment spontaneously or naturally. However, the true wine yeast is usually greatly outnumbered by undesirable organisms such as wild yeast and vinegar bacteria which seriously interfere with the desired fermentation.

In modern winemaking, undesirable microorganisms are killed or inhibited through the addition of small amounts of sulfur dioxide, potassium metabisulfite, or sodium metabisulfite to the fermenting vat. After 3 to 4 hours, a starter of actively growing selected yeast culture, which has been conditioned to sulfur dioxide and is well suited to the fermentation of grape must, is added and controlled fermentation proceeds. Agglomerating yeasts, including such strains as champagne and Burgundy, as well as nonagglomerating types of which Tokay is an example, are commonly used as wine starters in California. These strains and many others are in the collection of the Agricultural Experiment Station, University of California, and are available from commercial sources. The use of pure yeast not only permits controlled fermentation but yields a wine of superior flavor and quality in comparison with that produced by the yeast found naturally on the grape. Too, wines made with cultured yeast are more easily clarified.

Preparation of Yeast Starter. Selected pure yeast strains are grown in Roma's Fresno laboratory, used locally, and provided to Roma's other wineries. A stepwise procedure for propagation of yeast from standard agar slants to volumes of yeast starters required for plant fermentations is followed.

STEP 1. One hundred milliliters of grape concentrate, which has been diluted with water to 20° Balling, are placed in a 250-ml. Erlenmeyer flask. Flask and contents are sterilized in autoclave at 15 pounds' pressure for 15 minutes, cooled to 70° F., and inoculated by adding yeast growth from agar slant with sterilized inoculating needle. The flask is plugged and kept at room temperature (70° to 80° F.) for 24 to 48 hours; at height of activity, or when 50% fermented, the culture is used in Step 2.

STEP 2. One thousand milliliters of sterilized 20° Balling grape juice (diluted concentrate) are placed in a 2000-ml. flask, 150 p.p.m. of sulfur dioxide are added and inoculated with actively fermenting medium from Step 1. At height of activity it is used in Step 3.

STEP 3. Three thousand milliliters of sterilized grape juice prepared as above are placed in a 4000-ml. flask and inoculated with medium from Step 2. At height of activity, it is used in Step 4.

STEP 4. Medium from Step 3 is used to inoculate 3 gallons of fresh grape juice (22° Balling) in a 5-gallon glass jug.

STEP 5. Medium from Step 4 is used to inoculate 35 gallons of fresh grape juice in a 50-gallon stainless steel (Type 302) tank.

STEP 6. Medium from Step 5 is used to inoculate 350 gallons of grape juice in a 500-gallon iron, porcelain-lined tank.

STEP 7. Medium from Step 6 is used to inoculate 4000 gallons of grape juice in a 5000-gallon wax-lined concrete tank.

Temperature is controlled at between 70° and 80° F. in all steps. Sulfur dioxide is increased to 175 p.p.m. beginning at Step 3. Live steam is used to sterilize all yeast propagation apparatus beyond Step 3.

At this point, 5000 gallons of starter yeast are available and are pumped to concrete yeast tanks in the fermenting room containing approximately 15,000 gallons of grape juice sterilized with sulfur dioxide. This is used for starters in the various fermentation tanks the following day. A similar quantity of yeast starter is prepared and used each day.

TABLE V. YIELDS OF STEMS, POMACE, AND RAW WINE^a PER TON OF GRAPES

	Stems, Lb.	Pomace (Dry Basis), Lb.	Table Wine Equivalent, Gallons
Maximum	154	160	188
Minimum	40	40	141
Average	80	66	178

^a New table wines directly from fermenters. Normal yield of dessert wines would be approximately one half those shown.

Winemaking at the fermentation stage falls essentially into two broad divisions, red and white wines. In the making of wines having a red color, the juice is fermented on the skins. In the making of wines white (or amber) in color, the juice is fermented free of the skins. These broad divisions are further divided into table wines, dessert and appetizer wines, and sparkling wines. Table wines are normally fermented to a very small residual sugar content and contain not more than 14% alcohol by volume. In the production of dessert and appetizer wines, on the other hand, the sugar of the grape juice is only partially fermented, and, at the desired point, fermentation is

arrested by adding neutral grape brandy to between 19.5 and 21% alcohol by volume in the wine. Sparkling wines are produced by secondary fermentation of table wine.

Roma uses two types of fermenting vats or tanks. One type is an open tank 16 feet 10 inches square, 7 feet 6 inches in height, and made of reinforced concrete. Cooling is provided by three rows (132 linear feet) of 2-inch copper coils using cooling water at 72° F. There are 15 of these tanks of 16,000-gallon capacity each. The second type is a closed tank, also made of concrete. The largest tanks are 24 feet long, 22 feet wide, and 14.5 feet high, and have a capacity of 55,000 gallons each. Cooling is provided by six rows (345 linear feet) of 2-inch copper coils mounted on oak uprights. There are also smaller, closed concrete fermenters having capacities of 20,000, 25,000, and 30,000 gallons each. Tanks are treated with microcrystalline wax to limit corrosion.

In the making of red table wine, properly selected grapes are crushed as described and the must is pumped to the open fermentation tanks through overhead 6-inch copper lines. Three-way, quick-opening and quick-closing cast bronze must valves (15E) divert crushed grapes from lines to fermenting tanks through special rubber must hose. This special hose imparts no taste or color to the grape juice. Tanks are filled to three-fourths capacity or approximately 12,000 gallons of must. The fresh must is then immediately rendered commercially sterile by the addition of 100 p.p.m. of sulfur dioxide. Roma uses sulfur dioxide gas, which is bubbled directly from a cylinder through a rubber hose which is introduced by an operator to the bottom of the tank. A starter of fresh yeast is added in an amount equal to approximately 5% of the volume of the must. As fermentation proceeds, considerable heat is given off. The temperature is kept below 85° F. by circulation of cooling tower water through the cooling coils. This temperature control is important because, below 85° F., desired flavors are retained.

First visible sign of fermentation is appearance of liberated bubbles of carbon dioxide. These bubbles become entrapped in the skins, causing them to rise and form a hard cap on top of the fermenting must. This cap becomes very dense, often a foot or more in thickness. The temperature rises rapidly and heat-loving wine bacteria might grow in the cap unless it is broken up. This is done by pumping the liquid contents of the tank from a bottom valve and forcefully spraying it on the cap for 10 to 15 minutes, or until the cap is thoroughly broken up. This is repeated three or four times daily. Breaking up the cap also aids in the extraction of color from the skins. Complete fermentation requires from 7 to 10 days. During this time, the Balling has dropped to about 1°, indicating almost complete fermentation of the sugar to alcohol. The fermented juice is drained from the pomace and is allowed to flow by gravity over a mechanical screen containing $\frac{3}{32}$ -inch perforations. Pomace removed by the screen is conveyed to the pomace press and juice passes to a concrete sump, from which it is pumped to a closed fermentation tank to complete fermentation or until not more than 0.3% residual sugar remains.

White wines are fermented after the free-run juice is separated

TABLE VI. ANALYSIS OF SOME CALIFORNIA WINES

	Alcohol, % by Volume			Balling, Degrees at 68° F.			Total Solids, Grams/100 ml.			Reducing Sugar, Grams/100 ml. as Dextrose			Total Acidity, Grams/100 ml. as Tartaric Acid			Volatile Acidity, Grams/100 ml. as Acetic Acid		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
White table wines																		
Sauterne (dry)	11.0	13.8	12.0	-2.2	-1.4	-1.8	1.7	2.8	2.1	0.05	0.30	0.17	0.45	0.78	0.62	0.040	0.100	0.060
Sauterne (medium sweet)	11.0	13.9	12.5	0.0	2.0	1.0	3.8	5.7	4.8	1.0	3.0	2.60	0.45	0.75	0.60	0.040	0.100	0.066
Sauterne (sweet)	11.2	13.9	12.8	1.5	3.0	2.5	5.4	7.5	6.6	3.0	5.8	4.6	0.45	0.75	0.60	0.040	0.100	0.060
Rhine	10.8	13.5	12.0	-2.2	-1.6	-2.0	1.7	2.6	2.1	0.05	0.25	0.17	0.45	0.80	0.65	0.040	0.100	0.060
Red table wines																		
Claret	10.8	13.5	12.5	-1.6	-0.8	-1.2	2.2	3.4	2.6	0.10	0.40	0.28	0.50	0.85	0.60	0.050	0.110	0.065
Burgundy	11.0	13.6	12.6	-1.6	-0.6	-1.2	2.3	3.5	2.8	0.10	0.45	0.30	0.50	0.85	0.62	0.050	0.110	0.066
Zinfandel	10.9	13.5	12.4	-1.6	-0.6	-1.2	2.2	3.5	2.7	0.10	0.40	0.28	0.50	0.80	0.59	0.050	0.110	0.069
Dessert wines (white or amber)																		
Muscatel	19.5	20.5	20.0	5.5	10.0	6.5	11.7	16.0	12.6	0.30	0.50	0.42	0.025	0.070	0.040
Angelica	19.5	20.5	20.0	5.5	12.0	7.0	11.6	17.8	13.0	0.30	0.46	0.40	0.020	0.070	0.038
White port	19.5	20.5	20.0	5.5	8.0	7.0	11.5	14.0	13.0	0.30	0.44	0.38	0.020	0.060	0.035
Sweet sherry	19.5	20.5	20.0	3.0	7.0	6.0	9.1	13.4	12.0	6.6	11.4	9.8	0.35	0.55	0.46	0.035	0.065	0.048
Dessert wines (red)																		
Port	19.5	20.5	20.0	5.5	9.0	6.5	11.6	15.0	12.6	0.38	0.65	0.50	0.035	0.070	0.050
Tokay	19.5	20.5	20.0	3.5	6.0	4.5	9.5	12.2	10.6	0.38	0.52	0.44	0.035	0.065	0.050
Appetizer wines																		
Dry sherry	19.5	20.5	20.0	-3.2	-2.2	-2.5	3.0	4.3	3.9	0.5	2.4	2.0	0.32	0.58	0.48	0.030	0.070	0.050
Sherry	19.5	20.5	20.0	-1.4	-0.4	-1.0	4.8	6.0	5.4	2.6	3.9	3.3	0.32	0.50	0.45	0.030	0.065	0.048
Dry vermouth	18.0	20.0	19.0	-2.0	0.6	-1.0	3.8	6.8	5.1	0.48	0.75	0.62	0.028	0.060	0.045
Sweet vermouth	16.0	19.0	18.0	9.0	13.0	11.0	14.5	18.5	16.8	0.45	0.70	0.60	0.030	0.060	0.045
Sparkling wines																		
Champagne	11.5	13.5	12.4	-1.0	3.0	0.4	3.0	7.0	4.5	0.5	4.8	2.2	0.55	0.80	0.70	0.040	0.095	0.060
Pink champagne	11.5	13.2	12.4	-0.4	1.5	0.0	3.6	5.6	4.1	1.2	3.3	2.0	0.55	0.76	0.68	0.040	0.095	0.063
Sparkling Burgundy	11.0	13.0	12.0	0.0	2.0	0.5	3.8	6.2	4.7	1.4	3.6	2.2	0.55	0.80	0.72	0.045	0.100	0.068

from the skins, seeds, etc. Must from the crusher is pumped to a closed fermentation tank and sterilized with sulfur dioxide in the manner described for red wines. The free juice is then immediately allowed to drain from the vat and is pumped to a second fermentation tank where the yeast starter is added and the juice is fermented "dry." It is then racked to settling tanks in the storage cellar.

In making red dessert wines, in which the alcohol content of the finished wine ranges from 19.5 to 21% by volume, the open fermentation tanks previously described are used. Fermentation normally is allowed to proceed until the Balling of the grape juice has dropped to approximately 50% of its original value—as an example, 24° to 12°. Color is extracted from skins by pumping over as for red table wines. This requires 3 to 4 days. At this point, the juice is racked to fortification tanks where neutral grape brandy, ranging from 185° to 189° proof, is added to arrest the fermentation. Agitation is provided by air introduced to the bottom of the tank. The resulting alcohol content is approximately 20% by volume and the sweetness is retained at between 6° to 8° Balling.

White, as well as amber, dessert wines are usually produced in the same manner as that described for red dessert wines, except that the juice is normally fermented off the pomace. The exception is muscatel, which may or may not be fermented on the pomace. Sherries differ in their production from dessert wines in that the juice is fermented to the desired degree of dryness and then brandy is added until the resulting alcohol in the wine is approximately 20% and the residual sugar in grams per 100 ml. is as follows:

Dry sherry	Less than 2.5
Sherry	2.5 to 4.0
Sweet sherry	4.1 to 12.0

Wine bases for the appetizer wines, dry vermouth, and sweet vermouth are made approximately as outlined for dry sherry and white dessert wine, respectively.

PRESSING

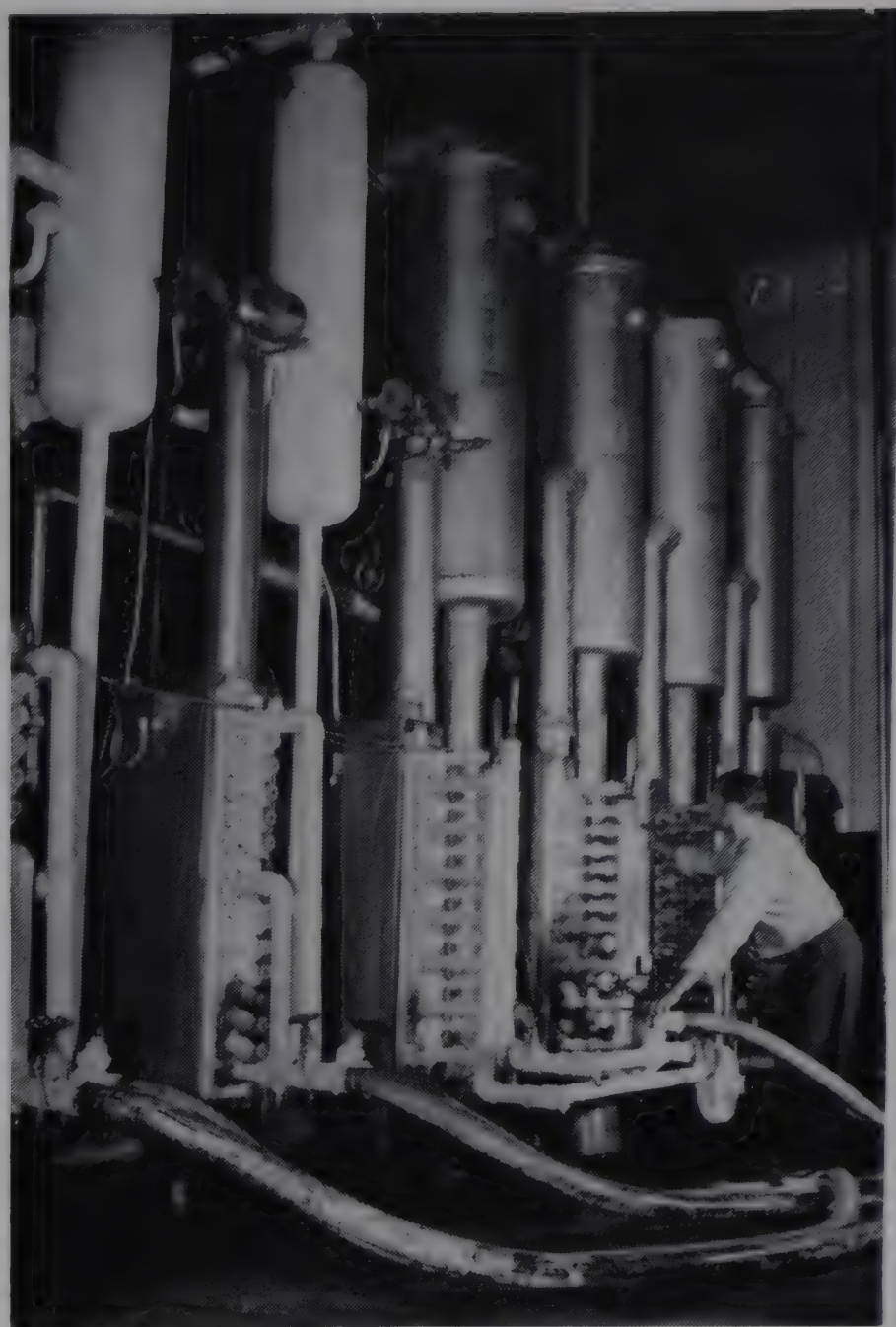
Wet, unpressed pomace constitutes 6 to 16% of the weight of the grapes crushed. It contains primarily skins, seeds, and wine, the quantities depending on the type of grapes crushed and fermenting conditions.

At Fresno, the free-run wine is allowed to drain from the pomace. Water is then added to the drained pomace and the mixture is fermented dry, producing a distilling material containing approximately 6% alcohol. This liquid is drained off and added to other distilling materials. Pomace is further leached with water until not more than 2% alcohol remains in the pomace, and these water washes are added to distilling materials. Pomace is removed from open fermentation tanks with portable sprocket and chain elevators equipped with hardwood cleats (16E). That in closed fermentation tanks is flushed with water to the main pomace conveyors. Pomace is transferred by a 24-inch underground drag chain conveyor to the press room.

Roma has four continuous screw presses of two sizes. These are twin screw units, the screws being 13 and 16 inches in diameter and made of cast alloy steel containing 4 to 6% chromium (17E). A positive pressure feed device in the feed hopper assures uniform pressure on the adjustable cones. Pomace is fed into the hopper at the top of the press, drawn immediately into the press chambers through the pressure feed device, pressed, and discharged. Press is operated by a 25-hp. high torque 100 r.p.m. motor through synchro gear reduction. Rated capacity for the 13 inch presses is the pomace from 40 to 50 tons of grapes per hour, and for the 16 inch presses is 50 to 70 tons per hour. The press cake contains from 50 to 70% moisture. Press liquid is pumped to distilling material storage tanks.

STORAGE AND PROCESSING

Before wine is ready for sale and consumption, it must be clarified, aged, and stabilized. During aging, it undergoes certain favorable changes in odor and taste that distinguish an old wine from a new one. Clarification is aided by fining and filtra-



Forty-Ton Ammonia Refrigerating Units Used to Cool Wine to a Temperature at Which Tartrates Precipitate

tion. When wine is subjected to extreme temperatures of summer and winter, tartrates and protein may precipitate, causing the wine to become hazy. As the American public demands brilliantly clear wine, stabilization (hot and cold) is necessary. Stabilization is achieved by refrigeration and if necessary heating, followed by filtration.

The completely fermented wine is racked from the fermenting tank to a settling tank where sedimentation of suspended solids, including yeast cells, albuminoids, tartrates, coloring matter, and pectinous materials, occurs. After 2 to 6 weeks, the wine is racked off the lees to storage tanks. Wine transfer pumps are used for movement of wine throughout the winery. These are chiefly Type 316 stainless steel 1800 r.p.m. centrifugal pumps operated by motors of various sizes. Capacity of one of the more common pumps ranges from 40 to 195 gallons per minute as the head decreases from 120 to 40 feet (18E). In all operations wine is conveyed by special wine hose or by stainless steel pipelines. This hose is wrapped in fabric and has a specially prepared tasteless and odorless inner tube. The stainless steel lines are either Type 302 or Type 304.

Fining. When finely divided solids are suspended in the wine and will not flocculate sufficiently to settle out, an agent is employed to assist in the removal of these solids. This operation is known as "fining." The fining agent causes the particles of suspended material to coalesce and settle out. Of the many fining agents used, the more important include gelatin, casein, and Wyoming bentonite.

Bentonite, a special montmorillonite clay with unusual swelling and other colloidal properties, has largely supplanted all other fining agents used in clarifying California wines (8). It was first used for the clarification of honey (13) and later used in vinegar making (14). In addition to being an effective fining

agent, bentonite is very easy to use. Available in powder or granulated form, it can be readily made up into a smooth suspension and added directly to the wine.

Roma adds bentonite in the form of a wine slurry at the rate of 1 to 5 pounds per 1000 gallons of wine, the exact amount depending upon the requirements of the wine being treated. After the bentonite with the suspended matter has settled, which usually takes from 7 to 8 days, the clarified wine is pumped from a valve above the sediment level to filters. The addition of bentonite in no way adversely affects the color, flavor, or bouquet of the wine.

Filtration. In the clarification of wine, filtration is a necessary supplement to settling, racking, and fining. The filters remove insoluble tartrates, yeast cells, and coloring matter not removed during earlier processing. Usually one filtration follows fining, one at low temperature follows refrigeration, and an additional filtration immediately precedes bottling. However, if necessary, additional filtrations are made.

A battery of eight plate and frame filter presses constructed of aluminum alloy is used in the Roma winery. Six are 36 by 36 inches in size with a capacity of 6000 to 8000 gallons per hour each, and two are 24 by 24 inches in size with capacities of 3000 to 4000 gallons each (9E). Special chain weave 21-ounce cotton filter cloth is used between the frames. Diatomaceous earth is used as a filter aid and is added continuously to the wine in mixing tanks preceding each filter. These are Type 302 stainless steel tanks, 36 inches in diameter and 36 inches high, equipped with agitating paddles (12E). The filter aid is added by an adjustable hopper at an average rate of 200 pounds per 100,000 gallons of wine. For unusually clear wines, the rate is 150 pounds; for turbid wines, as high as 400 pounds are used. A precoat of asbestos fiber is applied to the filter cloth in the case of polish or final filtrations. Wine is forced through the filter at 35 to 45 pounds per square inch pressure. Clarity of the wine is tested at the discharge end of each filter and checked at regular intervals with a Zeiss Pulfrich photometer using a turbidimeter attachment. Filter cloth is removed and cleaned of filter aid and other material when necessary, which normally is after every 100,000 gallons or at the end of 24 hours.

Refrigeration. In many winemaking countries, winter temperatures are sufficiently low to cause precipitation, during aging of the wine, of excess tartrates normally in solution which otherwise might not be removed prior to bottling. In other areas, including California, detartation is slow because of mild temperatures, and refrigeration of the wine to a temperature near its freezing point, resulting in the removal of tartrates in the minimum time, is the general practice. Some wineries store the cooled wine in tanks located in a cold room. Others refrigerate wine by pumping it from a large tank through a tubular refrigerator and returning it to the tank, recirculating until the desired temperature is reached.

Roma has six cold storage tanks, each with a capacity of 95,000 gallons. They are made of reinforced concrete and insulation is provided by a 4-inch layer of cork. The principal refrigerating system consists of six 40-ton ammonia refrigerating units which are used in pairs (2E). These are operated by 40-hp. 1800 r.p.m. compressors. Sweet wines are cooled to 18° F. and dry wines to 24° F. Feed temperature is usually approximately 60° F. and the refrigerating units require 48 hours to cool 95,000 gallons down to the desired temperature. Most wines are held in cold room for 2 weeks and for an additional like period if necessary. They are carefully filtered after refrigeration, at which time they are ready for pasteurizing if necessary and for additional aging. Various auxiliary refrigerating equipment is used for cooling wine when necessary. Included is a small cold storage room containing eight 5000-gallon holding tanks.

Blending. Nature makes no provision for uniformity of different lots of wine of the same type. In order that the color, body, flavor, aroma, and bouquet of any particular type and brand may always be the same, wines of different lots are blended. This is one of the most important cellar operations, and, through blending, wines which vary in acid, body, flavor, color, etc., are balanced to standard specifications.

By the time a particular lot of wine is ready for blending, a mass of data has been accumulated describing its properties. Each storage tank of dessert and table wine has been completely analyzed once a month, and, in addition, table wines have been given a partial analysis weekly. A partial analysis includes determination of volatile acids, free sulfur dioxide, total sulfur dioxide, and photometric and microscopic examinations. A complete analysis includes in addition determination of alcohol content, Balling or Brix, total acids, clarity, and, in some wines, iron, copper, and reducing sugar. In addition to the monthly and weekly checks, a complete analysis is also made after every treatment, including each racking, filtering, and fining.

As has been true down through the ages, taste tests are still the final and most important factor in determining whether or not a wine meets all quality requirements. Roma has a staff of long-experienced tasters. The laboratory staff first makes up small sample blends. If analysis of the blend is satisfactory and tasters agree as to its quality and uniformity (Roma requires unanimous approval of its three senior tasters or the blend is rejected), calculated volumes of the various component lots are transferred to a blending tank. After "pumping over" until well mixed, the blend is analyzed and again tasted to assure that the blend was made correctly.

Heating and Pasteurizing. Some wines, particularly muscatel, may contain an excess of albuminoids and proteins which would cause haziness at warm temperatures if not eliminated. They are removed by heating the wine to 130° to 150° F., at which temperatures these substances coagulate and precipitate. Pasteurization is used when necessary to kill wine yeast and bacteria.

Roma stabilizes its wines against cloudiness at high temperatures by heating the wine to 135° F. and following this treatment with water cooling to 80° F. A multiple-purpose plate and frame wine pasteurizer is used (1E). All parts of the pasteurizer which come in contact with wine are made of Type 304 stainless steel. The unit is also used for flash pasteurizing wine to 160° F. and, through a regenerative system, immediately reducing the temperature to 70° F. Water is used as a heating agent.

Wine may also be heated or pasteurized in tank-type pasteurizers equipped with steam heating coils. Roma has three 7000-gallon pasteurizers of this type. They are 7 feet 6 inches in diameter, 18 feet high, made of 3/16-inch stainless steel plate. Each has three Type 321 stainless steel coils 1 inch in diameter and 70 feet in length. Each unit is equipped with a preheater and heat exchanger. Insulation is provided by a 2-inch layer of 85% magnesia block. Tubular type steam pasteurizers constructed of borosilicate glass and Type 304 stainless steel are also used for wine pasteurization at Fresno.

Storage Tanks. Roma's storage capacity which is used for storing, aging, and finishing wine totals over 15,000,000 gallons. Tanks include concrete tanks ranging from 5000 to 215,000 gallons, redwood tanks ranging from 1000 to 50,000 gallons, and oak casks ranging from 500 to 9000 gallons each. Concrete tanks are used primarily for storage and processing, whereas the redwood tanks and oak casks are used for aging. During aging, each lot of wine has its own aging characteristic and the point at which it reaches full maturity is determined by periodic taste examinations. In general, the aging period may be from 1 to 5 years.

Sherry Baking. California sherries are distinguished by a "rancio" or nutty flavor which is the result of heating at low temperatures for long periods of time. The process is called "sherry baking." Roma has six 80,000-gallon concrete sherry baking tanks which are heated by steam in 1/4-inch Type 302 stainless steel coils. Pale dry sherry is brought to 115° F. and held for 6 months. Regular sherry is held at 125° F. for 4 months.

After baking, sherries are blended for uniformity in quality and again undergo the usual stabilizing processes.

Increasing interest has been shown in the production of California sherry by the flor sherry process in recent years. The

WINEMAKING

California's climate and soil are ideal for cultivation of *Vitis vinifera* grapes



Tasting is the final test of quality and uniformity of wines

One million bottles of champagne can be stored in this underground cellar



distinct bouquet and flavor of sherry made by this process are due to the use of a special group of film-forming yeasts called flor yeasts and through progressive fractional blending during aging. The process has been described in detail (9).

Vermouth. There are two types of vermouth, sweet or Italian and dry or French. The vermouth flavor is a result of the addition of numerous aromatic substances to the wine. These include herbs, barks, flowers, roots, leaves, and seeds, most of which are imported from throughout the world. Each producer of vermouth closely guards his formula of flavoring materials used in vermouth making.

In making dry vermouth, Roma uses a selected table wine to which has been added neutral grape brandy as for sherry but to only approximately 19.5% alcohol. This base is stabilized as for other wines and aged until ready to be used. Roma selects herbs and other flavoring materials from over 50 different botanicals. These are steeped in the wine until the desired flavor is achieved, which normally takes from 5 to 10 days. Redwood tanks, ranging in capacity from 2700 to 10,000 gallons each, are used. The vermouth is filtered from the herbs and is then aged and stabilized for bottling as in other wine processing. Alcohol content in the finished vermouth is 19.0% and residual sugar is 2%.

The base wine for sweet vermouth is fermented as described for white dessert wine, except that fermentation is not allowed to proceed as far and a higher sugar content is retained. Neutral grape brandy is added to give an alcohol content of 19.0%. The finished sweet vermouth contains 18.0% alcohol and a sugar equivalent of 11° Balling.

Champagne. Champagne is the most important of the sparkling wines. Its effervescence is due to an excess of carbon dioxide which has been absorbed during a second natural fermentation within closed containers. Choice white table wine is the champagne base. To it are added champagne yeast and sugar, and the mixture, which is called the "tirage," is placed in a closed container and the second fermentation proceeds.

BOTTLE PROCESS. In the older or bottle fermentation process, the container is 1 gallon or less, usually a $\frac{1}{5}$ -gallon champagne bottle. The bottles of fermenting champagne are stored horizontally in stacks for several months, at the end of which time fermentation is complete.

The clarification or separation of sediment formed during fermentation from the wine is accomplished by placing the bottles in a rack, neck down, and daily shaking and turning each bottle in a skillful manner until sediment is closely packed upon the cork. The next step is "disgorging," or removing the sediment from the bottle. This is accomplished by quickly freezing the neck of the bottle in brine, releasing the clamp that holds the cork, and permitting the pressure to force the frozen sediment from the bottle. A "dosage" or sweetening liquor consisting of sugar sirup, grape brandy, and wine is added at this point. In the case of Brut champagne, the dosage contains little or no sugar. The bottle is then recorked, the cork is wired on, and, after final aging, the champagne is ready for shipment and consumption.

CHARMAT PROCESS. Making champagne by the bottle fermentation method is tedious and expensive. In 1907, Eugene Charmat developed a bulk process which bears his name. In the bulk process, the container may be of any size above 1 gallon; however, fermentation is normally carried out in containers ranging from 500 to 1000 gallons. Champagne produced by this process is considered by many to be of a quality at least equal to that made by the bottle fermentation process. Roma makes champagne by the Charmat process.

The champagne department includes 41 double-jacketed tanks of 1000-gallon capacity each. Type 304 stainless steel is used in the construction of 25 tanks and the balance are Flexlined, or internally coated with a layer of glasslike acid-resisting material. The inner shell is made to withstand a pressure of 150 pounds per square inch and the outer shell contains jackets through which

cold brine or warm water may be circulated for temperature control.

A select table wine especially prepared for champagne is used as a base. To this champagne stock, a quantity of invert sugar sirup, which will give a pressure of between 4 and 5 atmospheres at 40° F., is added. One atmosphere of pressure requires the presence of 4.3 grams of sugar per liter, and the exact amount of sugar added is determined from this relationship. An active champagne yeast culture approximately 5% of the volume of the tirage is added. The tirage is thoroughly mixed, all valves are closed, and the second natural fermentation begins.

During fermentation, the temperature is maintained at between 62° and 68° F. for approximately 30 days. At the end of this time a dosage of sugar and brandy is added. Champagne is clarified by being cooled to 24° F. and standing for 4 weeks at this temperature. It is then filtered under isobaric conditions to a second like container. After resting for at least 30 days, it is bottled isobarically using a special champagne filling machine. Bottles are corked and wired, and are placed in an underground cellar for aging at 66° to 70° F.

Great care is taken in the making of champagne from the selection and crushing of the grapes to the finished product. During the second natural fermentation, temperature and pressure are observed at periodic intervals. After the third day, decrease in sugar is determined daily. Complete analyses, including taste tests, are made after fermentation is complete, after clarification, and after bottling and aging.

BOTTLING AND SHIPPING

Wine is shipped in bottles, barrels, railroad tank cars, and tank trucks. Approximately 60% of all wine made in the United States is shipped in bulk to consuming centers, where it is bottled by local branches of the producing company or by wholesalers (19). Savings in shipping cost for transcontinental and other long distance hauls explain the limited bottling at wineries, even though bottling at the winery may be more desirable. Since before World War II, however, bottling at the winery has been on the increase in California.

At Roma, all wines prior to shipping must pass a temperature stability test and are given a final polish filtration. Shipments are made both in cases and in wine tank cars of 6000- to 8000-gallon capacity. Bottle sizes include gallons, half gallons, quarts, fifths, and pints.

In the bottling operations, wine comes in contact with only stainless steel (generally Type 302 or 304), borosilicate glass, or special rubber hose. There are six fully automatic bottling lines and two semiautomatic lines having a total capacity of 22,000 cases in an 8-hour shift. Operations performed by machinery are: unscrambling or lining up of bottles dumped from cases, removal of case lint from bottles by air blower, filling, capping, and labeling. Manual operations are: placing of plastic seal on neck of bottles, inspection, and casing. Cases are automatically sealed and after the addition of federal tax stamps and serial number are conveyed to the warehouse. All bottling is subject to careful laboratory control. Three reference samples from each bottling line lot are kept for 2 years and checked periodically for stability or "shelf life."

BRANDY

Brandy is the distilled product of grape wine. Beverage brandy which is made for consumption as such is distilled at below 170° proof, aged in wood, and sold at a proof of 80° to 100°. Brandy used to arrest the fermentation in dessert wines is distilled at above 170° proof. This class includes neutral grape brandy or spirits fruit (grape), distilled between 170° to 190° proof; and neutral spirits fruit (grape) distilled over 190° proof. In the production of grape wines, only brandy or spirits produced from grapes or grape products may be used. In a dessert winery approximately one half of the total tonnage of grapes crushed is used for the production of brandy needed in



Concrete Storage and Processing Tanks

dessert and appetizer winemaking. The distillery is thus a very important division of such wineries. The distillation of wine and other grape products into brandy has been described in detail (3).

Roma produces both types of brandy. The distillery has four distilling material measuring tanks ranging from 50,000- to 164,000-gallon capacity each, constructed of concrete and lined with microcrystalline wax. There are two double-column continuous stills of copper construction (3E). Each unit consists of a 72-inch beer or stripping column and a 60-inch rectifying column. The beer column is 36 feet high, is made of $\frac{1}{8}$ -inch copper, and has a total of 26 plates. Twenty are perforated plates and six are plates fitted with 51 6-inch Barbet boiling caps. The rectifying column consists of seven sections each 60 inches in height, fitted with 2.5 by 0.625 inch steel rings. There are 46 bubble plates each having 33 6-inch Barbet caps. A dephlegmator, 42 inches in diameter, is fitted with cast bronze tube sheets 0.5 inch in thickness, and has 500 0.75-inch seamless drawn tubes 10 feet in length which are enclosed in a copper shell 0.125 inch in thickness. Condensers are of the same construction as dephlegmators, except that they are of the submerged type. They are 30 inches in diameter, 13.5 feet long, and are encased in a No. 14 gage copper shell. Each contains 300 0.75-inch copper tubes 12 feet in length. A countercurrent beer preheater 20 feet long and containing 20 5-inch copper tubes is provided. In the making of beverage brandy, only the equipment described is used. The product is distilled between 130° and 170° proof. The distilled brandy passes to receiving tanks, where it is reduced to 105° proof with deionized water, then barreled for aging.

In addition to the equipment described, an aldehyde column is used in producing spirits for use in making dessert and appetizer wines. The column is of copper construction, has 45 plates, and is 54 inches in diameter. It is heated by an external calandria and is equipped with dephlegmators and condensers. These brandies and spirits are distilled normally at approximately 186° proof and are used at this proof.

GRAPE CONCENTRATE

The production of pure grape concentrate, also called pure condensed grape must, is an activity of many wineries. The concentrate is used in the making of very sweet wines, or may be sold as such for other uses.

Roma has two vacuum pans equipped with external tubular heat exchangers for making grape concentrate. They are made of Type 304 stainless steel and the combined capacity of the two units is 600 gallons of product per hour (4E, 5E). Steam at 30 pounds per square inch and 275° F. is used in the heat exchangers. Unfermented grape juice at an average of 23° Balling enters the system at 110° F. It first passes through the heat exchanger and is then sprayed into the evaporating chamber which is operated at 120° to 130° F. and at a vacuum of 28 to 29 inches. Vacuum is provided by barometric condensers. Noncondensed gases are removed by steam ejectors. Juice is concentrated to about 70° to 72° Balling. From the vacuum pans it is pumped to wax-lined concrete storage tanks. The resulting concentrate weighs approximately 11.3 pounds per gallon and contains an average of 8.1 pounds of solids per gallon. It is shipped in drums with unmodified phenolic resin linings or in regular wine tank cars.

BY-PRODUCTS

Tartrates. Prior to World War II, virtually all the crude tartrates used in the United States were imported from foreign wine-producing countries. It was not until these sources were cut off that the California wineries found it economically feasible to recover these products. After the war, when low priced foreign imports again became available, most wineries discontinued recovery.

California grapes of *vinifera* varieties contain 0.8 to 1.2% total tartrate expressed as potassium bitartrate. Some of this precipitates on the walls and floors of fermenting and storage tanks and some during refrigeration. It is a relatively pure grade of potassium bitartrate ranging in purity from 80 to 90%. The bitartrate forms a hard layer attached to the tank walls. It can

be removed by chipping with hand or air chisels, loosened and blown off by direct steam, or dissolved with a strong alkaline solution. Roma removes it by applying direct steam through a special jet to the walls of the tank which causes the cream of tartar to loosen and fall off in large flakes. The bitartrate is sold as crude $\text{KHC}_4\text{H}_4\text{O}_6$ or argols.

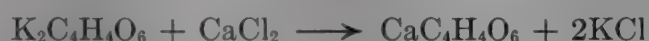
Most of the bitartrate is recovered from the lees deposited by the wine during settling and aging. Approximately 20 to 35% of dried lees is bitartrate. It does not have a market in this form because of its low purity. Roma runs the lees through a classifying centrifuge to increase its purity.

This is a continuous separating centrifuge with a capacity of 1500 pounds of dried bitartrate per hour (8E). Potassium bitartrate crystals ranging from 80 to 85% in purity separate out. Discharge from centrifuge, containing from 10 to 25% moisture, is dried in one of two steam-jacketed batch dryers, 4 feet in diameter and 12 feet long, which use steam at 70 pounds per square inch. The dryers have a capacity of 3000 pounds each and drying time is 5 hours. Product from the dryer, also identified as argols, contains 3 to 4% water or less and is sacked in 100-pound paper bags.

The Fresno winery expects to produce 400,000 pounds of this product in the 1951 season.

Much of the cream of tartar remains in the pomace after wine is racked and is leached out in the preparation of distilling materials. These tartrates can thus be removed as calcium tartrate either before or after distillation. Roma precipitates the product prior to distillation.

Heavy particles in the distilling material are allowed to settle out and the clarified liquid is pumped to 210,000-gallon concrete precipitating tanks. Calculated amounts of calcium chloride and lime based on the tartrates present are added to precipitate the tartrates and to adjust the pH to 4.5, since maximum yields of highest purity occur at this point. Reactions are:



The precipitated calcium tartrate is heavy and settles rapidly. Supernatant liquid is racked off and pumped to the distillery. The calcium tartrate precipitate is resuspended in water and pumped to one of three 8200-gallon redwood tanks. Approximately 200 p.p.m. of sulfur dioxide are added to destroy spoilage organisms. The tartrate is then centrifuged and dried.

Calcium tartrate is sold on a tartaric acid basis, minimum yield being specified as 50%. Roma has produced as much as 600,000 pounds of this by-product in a one-year period.

Pomace Stock Feed. Roma dehydrates its pomace, after pressing, to a low moisture content, grinds the dry product, and sells it as a livestock feed. Because of the crude fiber content, which is largely due to the seed hulls, the meal is best used as a supplemental feed, being mixed with molasses and concentrate for cattle.

A rotary, direct-fired gas drum dryer 8 feet in diameter and 60 feet long is used to dry the pomace (10E). Heat is provided by a gas burner and a fan located at the opposite end draws air through the kiln. Temperature of the flame is automatically controlled to maintain an exhaust air temperature of about 200° F. Pomace from presses enters the kiln with a moisture content of 50 to 70% and this is reduced to 5 to 6%. Light materials leaving the kiln with exhaust gases are recovered in a cyclone and returned to a screw conveyor which takes kiln discharge to a disintegrator of the type normally used in the feed industry (7E). Product from the disintegrator is 20-mesh. It is blown to a collecting cyclone and is sacked directly into 80-pound cloth bags which are then machine sewn. Analysis of the meal is:

Protein, %	12 to 15
Fat, %	6 to 9
Crude fiber, %	21 to 35
Ash (mineral matter), %	5 to 8

All pomace is disposed of in this manner and large undesirable accumulations common to most wineries have been eliminated. In 1950, the winery produced 1600 tons of grape pomace meal representing approximately 2.5% of the total tonnage of grapes crushed.

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- (16) Wine Advisory Board, San Francisco, Calif., "The Wine Industry," December 1950.
- (17) Wine Institute, San Francisco, Calif., *Wine Inst. Bull.* 500, 7 (November 1950).
- (18) *Ibid.*, 527, 8 (May 9, 1951).
- (19) *Ibid.*, 541 (Aug. 2, 1951).

PROCESSING EQUIPMENT

- (1E) Cherry-Burrell Corp., Little Falls, N. Y., superplate wine pasteurizer.
- (2E) Cyclops Iron Works, San Francisco, Calif., 800-gallon-per-hour wine cooler.
- (3E) Oscar Krenz, Inc., Berkeley, Calif., 72-inch split column continuous still.
- (4E) Oscar Krenz, Inc., side heating element type vacuum pans.
- (5E) Process Equipment Co., Los Angeles, Calif., vacuum pan.
- (6E) Rietz Manufacturing Co., Santa Rosa, Calif., pulp disintegrator RD-18-P.
- (7E) Rietz Manufacturing Co., standard feed disintegrator.
- (8E) Sharples Corp., Philadelphia, Pa., super-D-cantor classifying centrifuge.
- (9E) Shriver, T., & Co., Harrison, N. J., plate and frame filter presses, Catalog No. 38.
- (10E) Standard Steel Co., Los Angeles, Calif., 60-foot rotary kiln.
- (11E) Toledo Scale Co., Toledo, Ohio, motor truck scale No. 60-7032.
- (12E) Valley Foundry & Machine Works, Fresno, Calif., agitator No. 250.
- (13E) Valley Foundry & Machine Works, Model No. 240 rotary grape crusher, Catalog No. 47.
- (14E) Valley Foundry & Machine Works, Model No. 125 semidisplacement must pump.
- (15E) Valley Foundry & Machine Works, 6-inch must valves.
- (16E) Valley Foundry & Machine Works, 15-foot pomace elevators.
- (17E) Valley Foundry & Machine Works, twin screw pomace press Model DS-142.
- (18E) Valley Foundry & Machine Works, wine transfer pump Mode No. HH-141.

PLATINUM REFORMING OF GASOLINE

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Muskegon, Mich.

Prefractionator and stabilizer col-
umns with heat exchangers be-
tween them



WHEN petroleum first came into use in the late nineteenth century its producers and refiners found their major market in lamp oils; the heavier fractions were disposed of as lubricants, and the light naphthas were a sort of nuisance, with limited markets. It was not until after the turn of the century, as the internal combustion engine became an increasingly important power source, that gasoline became anything other than a by-product of kerosene production. Even in 1913 when the first commercial thermal cracking plant provided an effective method for rearranging the boiling point distribution of the crude fractions, the refiners were as much interested in increasing their kerosene fraction yield as they were in making more gasoline (12, 33). However, during the next 25 years the demand for high volatility, low flash-point fuels for use in the gasoline engine increased rapidly and soon overshadowed that for all other types of petroleum products. In recent years the increasing popularity of Diesel engines and the widening use of distillate heating oils has led to a comeback for the light distillate fraction so that since the early thirties the percentage rate of increase in demand for products in this range has exceeded that for gasoline products, Figure 1 (11). Nonetheless the annual increase in gasoline consumption is still impressive and the major research efforts of the petroleum

industry are currently directed in a broad sense toward obtaining the maximum gasoline from the residual oils boiling higher than gasolines and from the lighter gases boiling below gasoline. A concomitant objective is the improvement of gasoline quality so that it may be used in more efficient, high compression engines.

One of the basic characteristics of the internal combustion motor is that its energy efficiency varies almost linearly with the compression ratio of the combustion chamber. Recognition of this fact has led to a steady increase in the compression ratios of automobile engines. At higher combustion pressures there is a tendency toward detonation or premature ignition of the combustion mixture. The phenomenon is called "knocking" and the tendency is measured on an empirical scale of "octane numbers." Although several methods of determining this rating are used (5, 6), ratings cited in this article will be those determined by the "research method" (6) with 3 cc. of tetraethyllead added per U. S. gallon, unless otherwise stated, as this standard seems most closely related to actual road performance of high compression engines. Since its introduction, the octane rating has been the primary specification for motor fuel which must be met to produce an acceptable gasoline. Once the "octane race" was on, it was not sufficient to produce a fraction within the prescribed

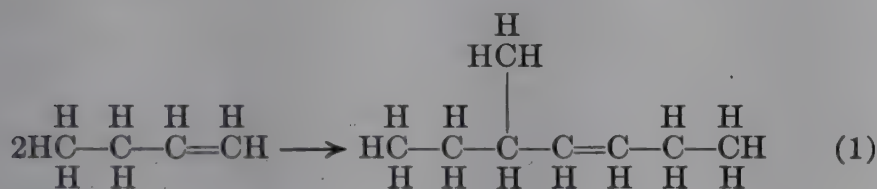
limits of vapor pressure and boiling range. The fuel, regardless of its crude oil origin, must have a combination of chemical properties which will ensure a certain level of knock-free performance.

There are about six types of gasolines produced in the United States, which, when blended together in various proportions, supply the needs of the motoring public (Table I). Straight-run gasoline, distilled directly from the crude, and natural gasoline, condensed in the production of natural gas, supply approximately 45 to 50% of the demand. Most of the remaining gasoline is produced from residual oils or light gases by thermal cracking (12), catalytic cracking (22, 31), polymerization (14, 23), and alkylation (24). The Platforming process described in this article was developed to improve the octane rating of the straight-run and natural gasoline.

GASOLINES FROM HEAVY OILS AND LIGHT GASES

Thermal cracking, the first process used commercially to rearrange the structure of molecules found in crude petroleum, produces a gasoline with an octane number higher than that of most natural or straight-run gasoline. The development of this process started the continuing progression of improved motor fuels and improved motor cars.

Part of the volumetric loss in the thermal cracking operation is represented by noncondensable gases. This gas has a substantial olefin content which can be polymerized catalytically at moderate pressures (500 to 1200 pounds per square inch gage) and temperatures of 400° to 500° F. (14, 23) or without catalyst at higher temperatures.



Solid phosphoric acid catalyst primarily is used for this reaction, although other acid catalysts have been used to some extent (25, 35, 36). The poly or polymer gasoline produced by this operation is high in octane number having a leaded rating of about 97. Polymer gasoline produced from isobutylenes and hydrogenated served as the first supply of 100-octane gasoline used by the allied air forces in World War II.

Alkylation (24) is sometimes used instead of polymerization. This process, by reacting the gaseous olefins from thermal or catalytic cracking operations with outside isobutane, produces a greater gross yield of high quality gasoline. Unless operated on a large scale where isobutane is readily available, it is not as economical as polymerization for motor fuel production (17). How-

TABLE I. APPROXIMATE GASOLINE PRODUCTION IN UNITED STATES REFINERIES^a

	Barrels ^b /Day	% of Total
Straight-run	743,000	30.5
Natural gasoline	420,000	17.0
Thermal cracked ^c	743,000	30.5
Catalytically cracked ^c	544,000	22.0
	2,450,000	100.0

^a Calculated from U. S. Bureau of Mines estimates for 1949.

^b Barrel of 42 gallons.

^c Includes polymer and alkylate.

ever, alkylation is widely used for the production of 100-octane aviation gasoline.

Catalytically-cracked gasoline has a higher octane rating than that which is produced by thermal processes. This, is because the concentration of low octane, unbranched, paraffin and naphthenic type compounds is lower in the catalytically-cracked gasoline, whereas the aromatic content is greater than in the thermally processed product. The processes produce about equal quantities of polymerizable olefins.

STRAIGHT-RUN AND NATURAL GASOLINES

Straight-run gasoline, the fraction distilled below 420° F. from untreated crude oil, varies widely in its properties. The octane number ranges from as low as 50 for gasoline from some Michigan-type crudes to as high as 85 for some California, West Texas, and Gulf Coast oils. Natural gasoline, a major portion of the liquid fraction condensed from natural gas, has an octane number varying from 65 to 75.

The performance requirements of modern motors are such that before these gasolines can be used satisfactorily in automobiles they must be blended with other gasolines of higher octane or be treated in some manner to improve their octane rating. A recent survey revealed that in some areas in the United States premium gasoline is now running about 91 octane rating, whereas regular is approximately 85.0 (15). Not only the straight-run and natural gasolines but also the thermally cracked fuels, with a rating of 75 to 85, fall below such market requirements.

Since there is very little market for low octane gasoline in the United States the problem of improving the performance characteristics of straight-run gasoline has confronted refiners for a number of years. The first remedy discovered was the addition of tetraethyllead (28) which will increase the octane rating of some straight-run gasolines as much as 20 points. The improvement varies with different types of gasoline, and this variation gives rise to another index—the lead susceptibility (21, 29).



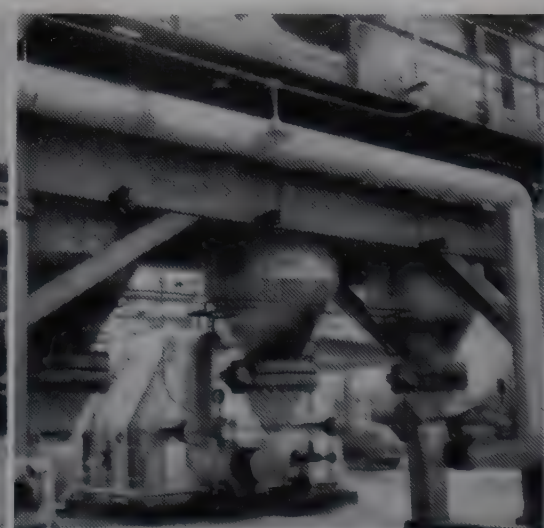
Motor-Driven Plunger Pump

Compresses feed up to 600 pounds per square inch operating pressure



Feed Heater

Originally constructed as a thermal reformer



Reactors

Lower ends are cooled by ring of steam jets

DESULFURIZATION

From the earliest days of petroleum processing, refiners had used various processes to eliminate the mercaptan odor, the obvious purpose being to please the nose of the consumer. When octane numbers became important it was discovered that desulfurization improved the lead susceptibility of gasoline (32). Early practice eliminated mercaptans by extraction with caustic soda in the presence of certain solvents (16, 26, 1A) or by treatment with sulfuric acid, and these processes are still used to some extent. In the late thirties catalytic desulfurization was introduced in which vapor phase treatment with clay or bauxite (7, 9, 10, 27), at temperatures of 750° F. or higher, removed mercaptans almost completely and up to 60% of the total sulfur in most straight-run gasolines. These processes can be effected at fairly low capital and operating costs and result in a minor loss in volume. However, at best, desulfurization will raise the leaded octane number of the gasoline no more than 6 or 7 points.

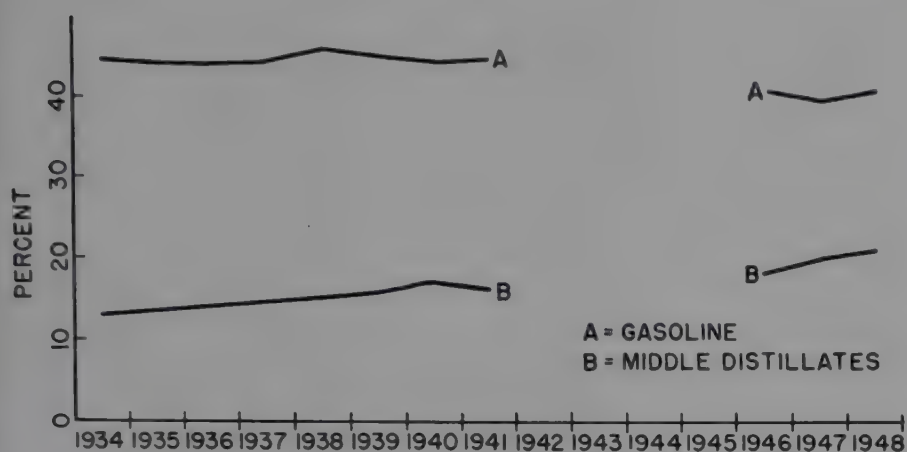


Figure 1. Percentages of Crude Oil Processed into Gasoline and Middle Distillate Fractions in the United States (11)

By increasing the temperature and time of the clay treatments, some molecular rearrangement or reforming of the crude naphtha may be attained and additional octane improvement realized (19). However, this process causes rapid loss of activity in the catalyst and consequently requires the installation of expensive regeneration facilities.

If the octane rating of the untreated gasoline is such that the improvement afforded by desulfurization is sufficient to meet market demands or if a higher octane material is available to blend with the desulfurized fractions, these processes may be adequate.

TABLE II. COMPARISON OF YIELDS IN REFORMING OF 200° TO 400° F. MID-CONTINENT NAPHTHA, 35 MOTOR CLEAR OCTANE NUMBER

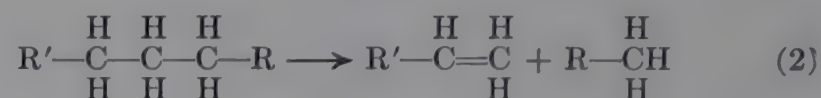
	Thermal Reforming	Thermal Reforming plus Polymerization	Polyforming	Hydroforming	Platforming ^a
Yield, 10 lb. vapor pressure (5), volume %	66	80	80	84	95
Outside butane required for 10 lb. vapor pressure product (5), vol. %	0	2	0	6	4
Total yield, vol. %	66	82	80	90	99
Octane ratings					
Motor method (F-2) (3)					
Clear	75	75	75	75	75
With 3 cc. TEL	84	84	85	86	87
Research method (F-1) (4)					
Clear	85	85	86	81	80
With 3 cc. TEL	93	93	93	93	93

^a Data from pilot plant of Universal Oil Products Company.

REFORMING PROCESSES

When it became evident that the addition of lead plus desulfurization were inadequate to produce a gasoline of an octane rating sufficient to meet the demand of the market, various processes were developed to rearrange the molecules of the straight-run gasoline to produce compounds having more desirable combustion characteristics.

The first such process, introduced about 1931, was thermal reforming which is primarily the adaptation of the cracking reaction to the gasoline fraction. If heated at an adequate temperature for a sufficient length of time, all hydrocarbons can be cracked. In general, the paraffins are somewhat more susceptible to this reaction than the other gasoline constituents, and there is a definite increase in cracking susceptibility with increasing boiling point. The liquid products of paraffin cracking have improved octane numbers both because they are lower in molecular weight and because they are partially unsaturated.



There is a relatively steep rise in the first part of the yield-octane curve for thermal reforming Figure 2. Unfortunately, this slope is not maintained because once the majority of the heavy paraffins have been cracked, increasing the severity of operation produces mostly light gaseous hydrocarbons. The falling off of the curve usually occurs at a yield of 80 to 85% with octane numbers ranging between 75 and 85. Some feed stocks can be thermally reformed to as high as 90 octane, but the yield drops to 70% or lower (Table II).

The volumetric loss in thermal reforming is almost entirely represented by noncondensable gases of much the same composition as those produced by thermal cracking. Modern practice, therefore, has been to combine a thermal reforming and polymeri-

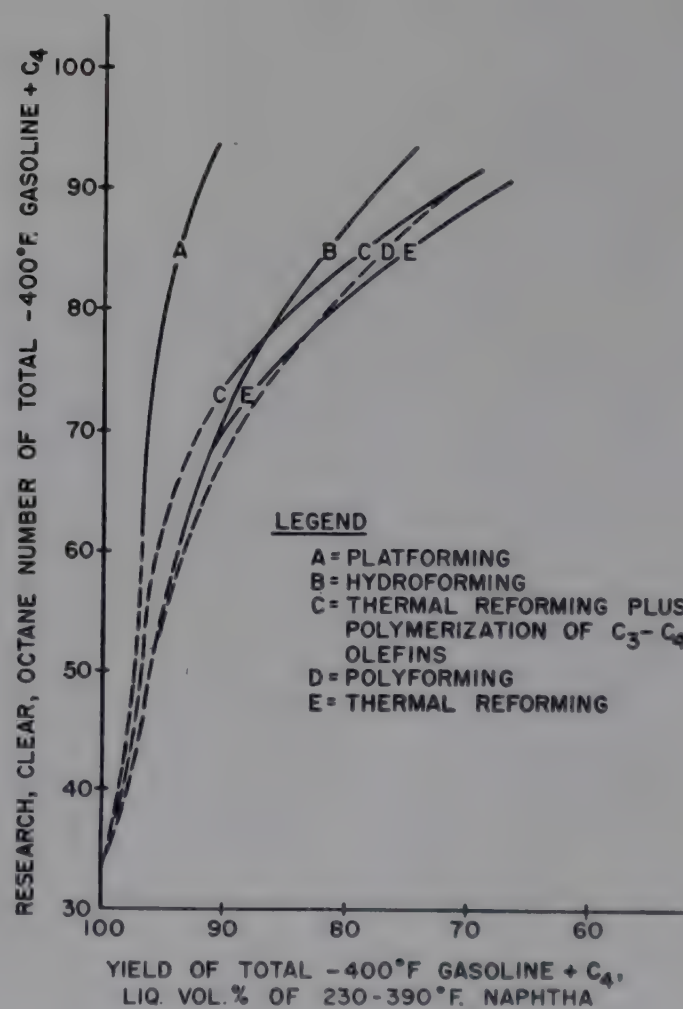


Figure 2. Yield-Octane Relations in Reforming Mid-continent Straight-Run Naphtha (53° API, 230-390° F.) by Different Processes

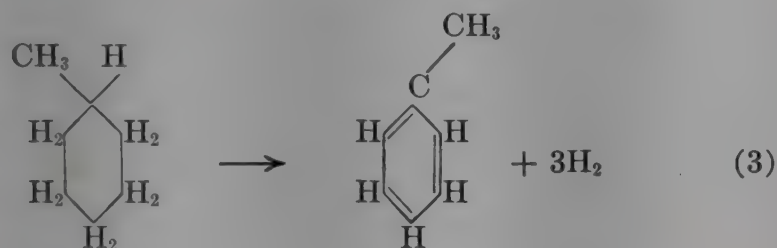
zation process to produce the best yield of high octane gasoline. In order to reach present-day octane levels with this type of operation, the production of polymer is as much as 15 to 20% of the total product. Only a few stocks will produce a high octane product by this combination of processes. Increasing the intensity of thermal conversion to produce a higher octane primary product increases the total volume of gas produced as the net gasoline yield decreases, but the concentration of polymerizable olefins in this gas is reduced as the increased temperature and time tend to crack the gaseous olefins to methane, ethylene, and ethane. Thus, the increased make of polymer gasoline under these conditions is not sufficient to replace the yield of gasoline lost, and the combined yield-octane curve levels off about eight numbers above the curve for thermal reforming alone.

POLYFORMING

The yield-octane curve is slightly improved by combining thermal reforming and polymerization into a single operation called polyforming (30) in which the off-gases are recycled to the reforming zone at pressures of about 1200 pounds per square inch gage and 1050° F. to force them to polymerize with the higher hydrocarbons. Although the reactions involved are fairly complex, the yield-octane limitations are about the same as for thermal reforming plus polymerization.

HYDROFORMING

Hydroforming is a completely different approach to the problem of octane improvement (8, 20). The primary reaction involved is the dehydrogenation of naphthenes, or saturated cyclic hydrocarbons, into aromatic compounds.



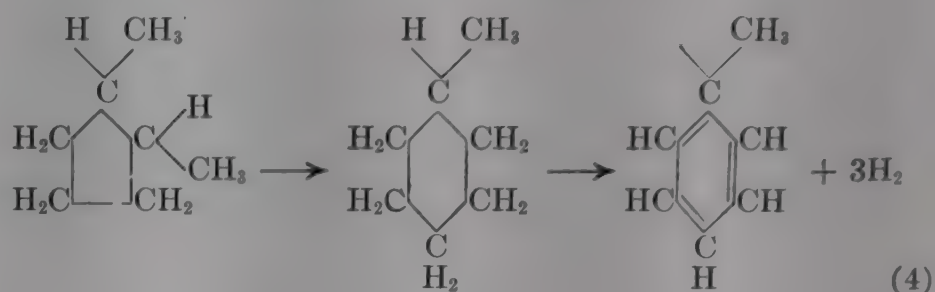
Cyclization of straight-chain hydrocarbons also occurs along with saturation-polymerization of any olefins which may be present. Hydroforming is accomplished catalytically with supported molybdenum oxide catalyst. Hydrogen is circulated over the catalyst bed in a mole ratio around 3:1 calculated on the feed. The reaction is accompanied by the formation of a substantial amount of tar or "carbon" which deposits on the catalyst and necessitates frequent regeneration. Commercial installations run on cycles of from 6 to 9 hours, half of the cycle being devoted to purging and regenerating with hot flue gas to which oxygen has been added. As a result, hydroforming reactors are always installed in pairs, to be operated alternately. In hydroforming, as in thermal reforming, the principal by-product is light gas. In this case, however, the gas is mostly saturated and cannot be polymerized. The yield-octane curve for hydroforming is somewhat better than for thermal reforming plus polymerization (Figure 2). However, the double reactors and complicated switch valve system require about 60% more capital investment than either polyforming or thermal reforming plus polymerization, and the complexity of the operation entails comparably higher operating costs. The process, although originally designed for octane improvement, has found its greatest use in the production of toluene (18).

PLATFORMING

A year ago last month, Universal Oil Products Company announced a new catalytic reforming process using a platinum catalyst developed by Vladimir Haensel. Dubbed "Platforming" for obvious reasons, the process combines the conversion of naph-

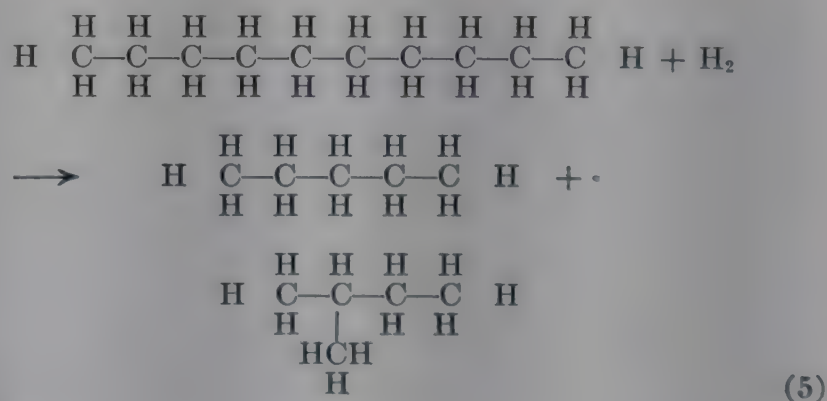
thenes to aromatics, the hydrocracking of paraffins, isomerization of paraffins, and virtually complete desulfurization into a single nonregenerative catalytic process.

Dehydrogenation of naphthenic hydrocarbons to aromatic hydrocarbons in Platforming follows the same reaction (Equation 3) found in hydroforming. Straight-run and natural gasoline usually contain a substantial amount of naphthenic hydrocarbons including those of both the six-membered ring and five-membered ring types. In the case of the latter structure, the dehydrogenation reaction is preceded by the isomerization reaction:



Under Platforming conditions dehydrogenation is highly endothermic and occurs very rapidly. Three moles of hydrogen are produced by each mole of naphthene aromatized. The reaction also results in some volumetric shrinkage because the aromatic product is more dense than the parent naphthene. Thus, for example, if the charge consisted of pure methylcyclohexane and if it were all converted to toluene, the theoretical yield of toluene would amount to 83.3% by volume of the charge. In this case, the octane number increase would be about 50 units. The naphthene content of straight-run gasoline varies considerably, but assuming an average value of about 40%, the theoretical volumetric yield after complete dehydrogenation would be about 93% if there were no other reactions. At the first commercial Platforming unit, described in this article, naphthenic compounds which can undergo dehydrogenation represent about 22 weight % of the charge.

The effects of hydrocracking in Platforming are the opposite of those that are the consequences of dehydrogenation. Hydrocracking results in a decrease in density and absorbs a part of the hydrogen which is liberated in the dehydrogenation reaction. The reaction is exothermic and provides some of the heat of reaction required for the dehydrogenation step, but it proceeds less rapidly. Hydrocracking involves the decomposition of high molecular weight hydrocarbons into lower molecular weight compounds, but it is not the same as thermal cracking or catalytic cracking, wherein paraffins are cracked indiscriminately along the hydrocarbon chain to produce lower boiling paraffins and olefins. Hydrocracking can be considered as a simultaneous cracking-isomerization-hydrogenation reaction.



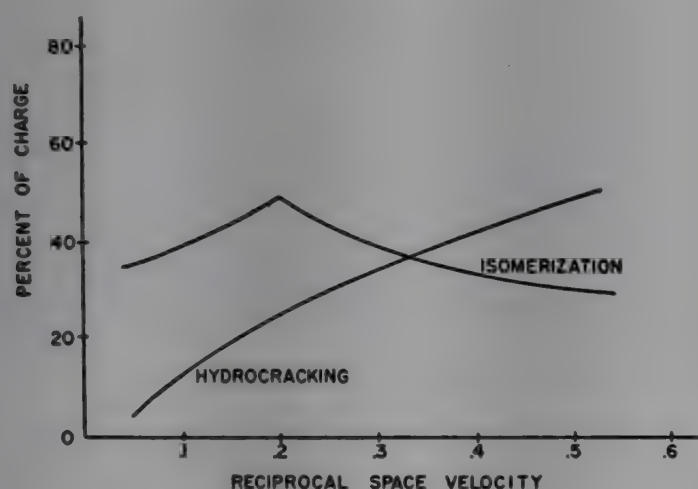
In practice, the break in the molecule does not occur only in the middle. Propane, butanes, hexanes, and heptanes are always formed along with the pentanes. Assuming that two pentane molecules are formed from decane, as in Equation 5, the volumetric yield at 100% conversion would be 118%. The octane number would increase more than 100 units in this assumed case

TABLE III. DISTRIBUTION OF ISOMERS PRODUCED IN PLATFORMING *n*-HEPTANE

(Space velocity 6; see Figure 3)

Compound	% in C ₇ Cut, Excluding <i>n</i> -C ₇ H ₁₆
	46.2
	30.6
	10.9
	4.7
	4.5
	3.1

because *n*-decane has a negative octane number to start with. Since the propane and lighter hydrocarbons formed along with the pentanes are lost as gases, only a part of the theoretical gain in volume and octane number can actually be realized.

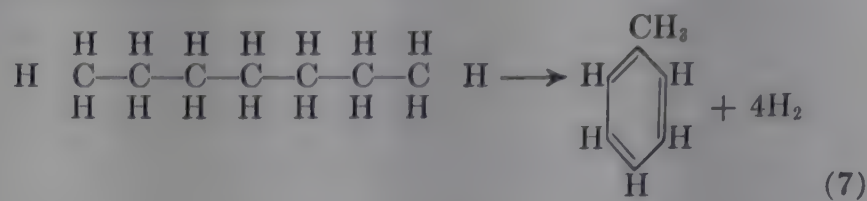
Figure 3. Relative Rates of Isomerization and Hydrocracking in Platforming *n*-Heptane

In addition to the isomerization of five-membered naphthene rings mentioned earlier, paraffins isomerize readily under platforming conditions to yield almost every possible isomer (Table III). In the case of *n*-heptane, this reaction proceeds faster than hydrocracking (Figure 3). As the space velocity is reduced, the extent of isomerization reaches a maximum value at a space velocity of 5. At lower space velocities, the hydrocracking of the isomerized compounds reduces the net yield by producing propane and butane which are lost as gases. The *n*-butane-isobutane ratio in the butane fraction is about 1.

Desulfurization is effected in Platforming by what might be considered a form of hydrocracking with the molecular fission occurring between the sulfur and carbon. The sulfur is usually removed as hydrogen sulfide, thus consuming 2 moles of hydrogen for each mole of sulfur compound eliminated. When naphthas from high sulfur content crudes are processed, this reaction has considerable economic importance since it eliminates the need for a separate desulfurization unit.



Some dehydrocyclization also occurs wherein paraffins are converted directly to aromatics.



PROCESS VARIABLES

The temperature, space velocity, pressure, and hydrogen recycle rate at which the reactions take place have a marked influence on the qualities of the platformate produced. As might be expected, the relationships between these variables are extremely complex, and it would not be practical in this paper to discuss the many details which are necessary to obtain a satisfactory correlation of operating conditions. Qualitative effects of changes in these variables can be shown, but it must be remembered that in actual operations the quantitative effects are influenced greatly by the type charging stock processed. Further, when a major variable is changed in the plant, it is usually necessary to make an adjustment in one or more of the other variables to obtain optimum over-all performance.

Table IV shows the effect of temperature change in processing straight-run stock from mixed paraffinic and naphthenic crudes. These results indicate that Platforming is a relatively low temperature operation and primarily catalytic, with few undesirable thermal effects. The results also indicate an increase in aromatization and hydrocracking with increased temperature. Since both reactions contribute substantially to the octane number gain, it is not surprising that increasing the process temperature increases the octane number of the product.

The effect of pressure as a major variable is indicated in Table V. Low pressure operation produces the most aromatics and the least amount of hydrocracking. At the highest operating pressure shown, 900 pounds per square inch gage, a large part of the octane number improvement is due to the hydrocracking reaction, since in this case the amount of hydrocracked material (as measured by the percentage over at 212° F.) is almost twice that obtained at the lowest pressure. Thus, by varying operating

TABLE IV. EFFECT OF TEMPERATURE ON PLATFORMATE

	Charge ^a	Products			
Av. catalyst temp., ° F.	...	813	843	873	903
Yield of C ₄ ⁺ , liquid vol. %	100.0	98.0	96.8	95.0	91.6
Vapor pressure at 100° F. (δ)	5.5	6.0	6.7	8.3	11.4
Research octane No., with 3 cc. TEL	80.2	85	88	92.5	98.5
Aromatics in product, %	9	19	27	35	45
Over at 212° F., %	31	34	36	41	46
Hydrogen production, cu. ft./bbl.	...	166	318	420	466

^a Initial boiling point to 350° F. mid-continent naphtha.

TABLE V. EFFECT OF OPERATING PRESSURE ON PLATFORMATE

	Charge ^a	Products		
Pressure, lb./sq. inch gage	...	500	700	900
Yields, vol. % of charge:				
C ₄ ⁺	...	92.6	92.9	93.2
C ₅ ⁺	...	86.5	86.1	83.5
10-lb. vapor pressure platformate	...	97.3 ^b	96.4 ^c	92.4 ^d
Research octane No. of 10-lb. vapor pressure platformate with 3 cc. TEL (δ)	52.8	95.2	94.3	94.9
Aromatics, based on charge, %	7.1	53.9	47.9	45.4
Over at 212° F. + loss, %	0	12.7	18.9	22.7
Hydrogen production, cu. ft./bbl.	...	685	488	287

^a 247° to 404° F. mid-continent, straight-run naphtha.^b With 4.7% outside butane.^c With 3.5% outside butane.^d Slight excess butane produced.

pressure, the Platforming operation can produce either a highly aromatic, low volatility gasoline, with high hydrogen production, or a more volatile product with a lower aromatic content and lower hydrogen production.

The upper pressure limit is determined by the point at which increasing thermal reactions cause the yield-octane relationship to deteriorate. The lower pressure limit is set by the minimum amount of hydrocracking desired as well as by the possibility of carbonizing the catalyst. Under normal operating conditions, carbon formation on the catalyst is prevented by maintaining a substantial excess of hydrogen in the process stream.

It has been pointed out that dehydrogenation has a high rate of reaction whereas hydrocracking is considerably slower. A study of the effect of changes in space velocity substantiates this statement. Table VI shows the results obtained in processing a mid-continent naphtha at various conditions in which space velocity was the principal variable. A change in space velocity from about 5 to 2 increased the extent of hydrocracking threefold (as measured by percentage over at 212° F.), but the aromatization reaction, already very extensive at the highest space velocity, was affected only slightly.

From these results, obtained in Universal's pilot plant, it is apparent that by small variations in operating conditions, it is possible to obtain a wider variety of volatility-octane relationships than is possible in thermal reforming.

OLD DUTCH UNIT

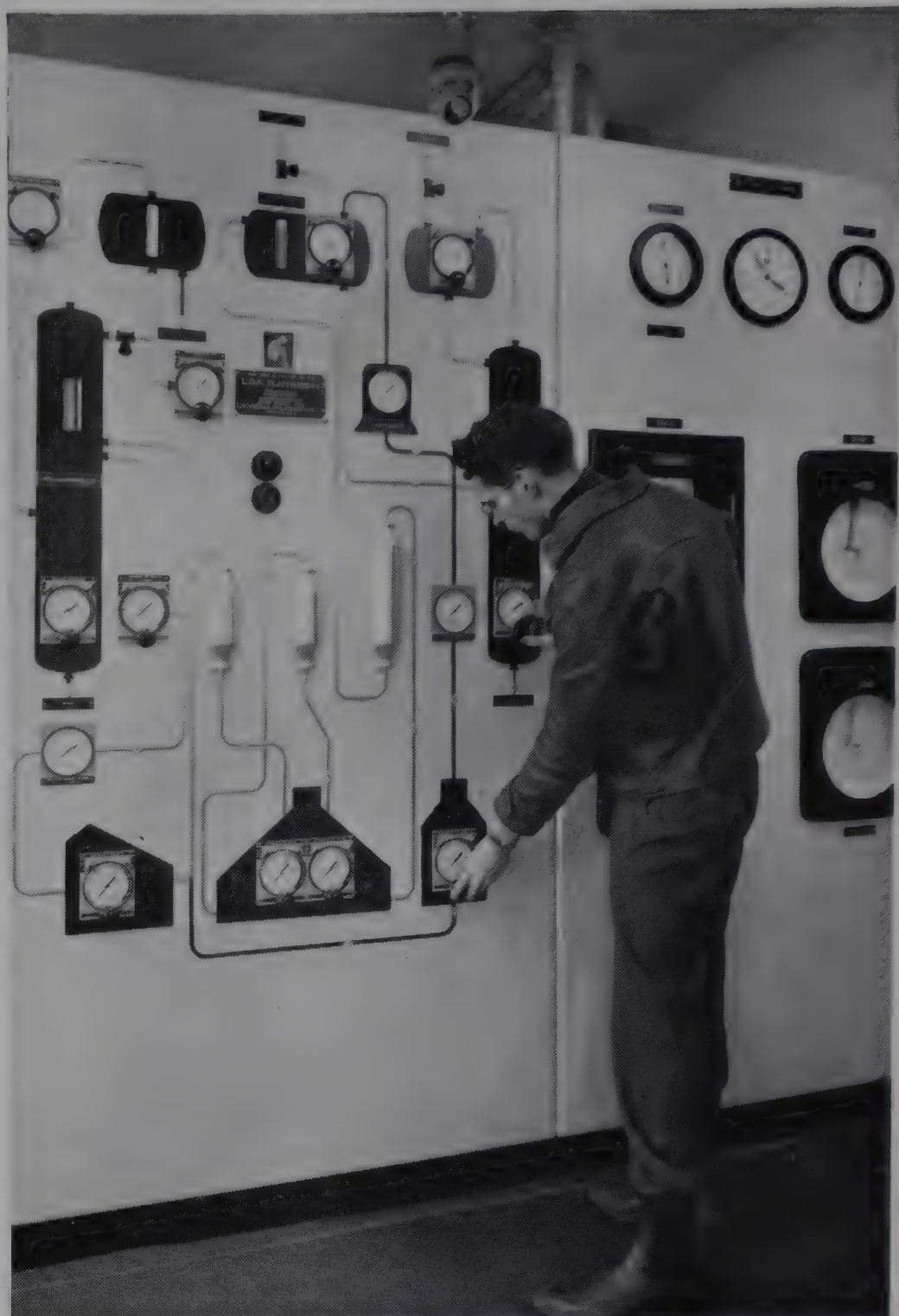
Shortly after the announcement of the availability of the process, the Old Dutch Refining Company of Muskegon, Mich., contracted for the construction of a Platforming unit. The installation was constructed in 139 days and completed in October 1949. Other units of the same type are now under consideration, but it is the pioneer Old Dutch operation which will be described in this article.

The Platforming unit (Figure 4) as constructed for the Old Dutch Refining Company is essentially in three separate sections. These sections are the feed preparation section, the reaction section, and the product fractionation section.

Feed Preparation Section. The arrangement and design of the feed preparation section can be varied considerably to integrate with existing facilities at the refinery where the platformer is installed. In general, the purpose of the prefractionator is to remove the lower boiling components of the straight-run gasoline. The only improvement in octane rating which can be obtained from the pentane and butane fractions is due to a partial isomerization. The extent of this reaction is usually not sufficient to justify the inclusion of these materials in the charge to the Platformer. The C₆ boiling range on the other hand in-

cludes five-membered naphthenes and six-membered naphthenes, as well as low octane, normal paraffins so it is usually advantageous to include material boiling in the C₆ range (160° to 180° F.) in the stock to be Platformed.

In addition to removing the low boiling material from the gasoline charge, the prefractionator permits control of the high boiling end point of the charge to the reactor section. The control of end point on this column is incorporated in the column design at relatively low cost and serves mainly as insurance against upsets in the crude oil still which might pass high boiling fractions into the reactors. In normal Old Dutch operation, the feed to this column is a mixture of naphtha and straight-run gasoline obtained from the distillation of crude oil. It is fractionated to remove overhead all material boiling below 200° F. The total overhead is condensed in a water-cooled condenser and collected in a reflux drum. Water, representing about 0.1% of the weight of the charge, settles out and is drawn from the reflux drum. The reflux is flow-controlled at a rate of approximately one to four times the feed. Reflux ratios at Old Dutch are calculated on a mole-ratio basis. Average molecular weights used for determining these ratios are estimated from boiling point distribution and specific gravities (34, 37, 38). The net overhead is taken from the reflux drum through a level operated control



Graphic-Type Control Panel

Although fairly common in some other chemical industries, this type panel is relatively new in petroleum refining

TABLE VI. EFFECT OF SPACE VELOCITY ON PLATFORMATE

	Charge ^a	Products			
Hourly liquid space velocity, vol. liquid/vol. catalyst ...		4.9	3.9	3.0	1.9
C ₄ ⁺ yield, vol. % ...		95.6	95.4	95.1	94.1
Vapor pressure at 100° F. (5) ...		4.5	5.2	6.4	6.9
Research octane No., with 3 cc. TEL	59.5	86	89	90.5	93
Aromatics in product, %	7	37	39	39.5	41
Over at 212° F. + loss, % ...		8.3	13.5	16	24
Hydrogen production, cu. ft./bbl.		495	475	470	430

^a 230° to 395° F. mid-continent naphtha.



Figure 4. Flow Sheet for Platforming of Gasoline in 1500-Barrel-per-Day Unit at Old Dutch Refining Company, Muskegon, Mich.

valve and is returned to the other sections of the refinery for stabilization and removal of hydrogen sulfide and mercaptans before blending into product gasoline. Sometimes this overhead is recombined with the platformate as it comes from the reactors before stabilization and hydrogen sulfide removal. However, it was found expedient at Old Dutch to stabilize this overhead in other sections of the refinery.

The charge to the reaction section (200° to 375° F.) is taken from below the fourth tray (from top) of the 18-tray prefractionator. The section of the column from which this material is drawn is known as the center well and is designed to permit passage of vapors while maintaining a surge capacity to absorb minor variations in the column feed rate. The lower section of the column is refluxed with liquid from the center well, flow-controlled at a rate approximately one fourth of the column feed rate. Bottoms from the prefractionator comprise a kerosene fraction boiling between 375° and 550° F. which is withdrawn through a level control valve and pumped back to the crude still. This bottoms cut could be taken above 400° F. or even 425° F. without seriously impairing the octane rating of the platformate. However, in the market area of Old Dutch, demand for kerosene is particularly strong and this bottoms cut is highly salable in its untreated form. Under other conditions the heavier bottom cut might be marketed as Diesel fuel or light distillate fuel. This reservoir of bottoms held in the still circulates through an exchanger to absorb heat from the reactor products. No other external heat is necessary to accomplish the prefractionation.

Reactor Section. The hydrocarbon charge to the reactor section is pumped to reactor pressure (700 pounds per square inch gage) by a motor-driven, plunger pump (2A) preheated by part of the reactor product, and passed into a gas and oil fired naphtha preheater. This heater was built as a thermal reformer and was available on the plant site when the Platforming unit was being designed. To adapt it to its new functions it was only necessary to remove the tubes from what was formerly the "soaking" section. The furnace is fired so that there is a minimum time at high temperature. The heated hydrocarbon vapors are joined by recycle hydrogen, heated to the same temperature, and enter the first of three adiabatic reactors. As the combined reactions are endothermic and sensitive to temperature change, it is necessary to add heat between reaction zones. The heat requirement is greatest in the first reactor and decreases progressively until the final reactor operates at very nearly isothermal conditions.

The reformed product from the third reactor is split into three parallel streams. One stream is cooled in exchangers with the recirculating bottoms from the prefractionator and the feed to the prefractionator, consecutively. The second stream is passed successively through an exchanger with the recirculating bottoms from the stabilizer column and the feed to the naphtha preheater. The third stream by-passes the stabilizer reboiler and joins the second stream before it enters the naphtha preheater feed exchanger. The flow is divided among the three lines by automatic controls. The two lines passing through the distillation reboilers automatically take enough flow to maintain proper temperature in the column bottoms. Temperature-operated throttle valves control this flow. The remainder of the flow goes through the by-pass. After these exchanges the streams are recombined and used to heat the recycle gas from the compressors before

being condensed in a water-cooled condenser and collected in a product receiver at approximately 100° F. and full reactor pressure. This type operation uses a minimum of exchanger surface while making the unit almost completely independent of outside sources of heating.

The gas and liquid portions of the reactor stream separate in the receiver. The gas is taken from the top of the drum and the major part is recycled by a single stage motor-driven compressor (1A). The recycle gas is reheated by exchange with the reactor product and passes through a tubular gas-fired heater before joining the hydrocarbon stream entering the reactor. The net make of gas, containing hydrogen with equilibrium amounts of methane, ethane, propane, and butane, is released through a pressure control valve discharging to the fuel system of the refinery. Under all conditions some excess hydrogen is produced, although the amount will vary with the nature of the feed and the severity of operating conditions.

The liquid product from the receiver is discharged through a level control to the product stabilizer.

Product Stabilizer. This fractionating column is operated to remove any remaining hydrogen and hydrocarbons of molecular weight lower than butane from the liquid fraction of the reactor effluent; it maintains a constant vapor pressure of the bottoms product.

The feed to the stabilizer after picking up heat from exchange with stabilizer product enters at the fourteenth tray of the 24-tray column. The stabilizer operates at approximately 300 pounds per square inch gage with a top temperature of approximately 130° F. and a bottom temperature of 460° F. The overhead is cooled in a water-cooled exchanger and the liquid and vapor are collected in a reflux accumulator. The net overhead vapor is discharged through a pressure control valve to the absorber section of the refinery's thermal cracking unit. This off-gas consists of hydrogen, hydrogen sulfide, methane, ethane, propane, and butane. Butane and part of the propane are absorbed and the remainder of the light gas is used as refinery fuel. The column is refluxed at a constant rate which is approximately 1.4 times the feed rate. As there is no net liquid draw-off from the reflux accumulator, the liquid level is controlled by the temperature of the accumulator.

The bottoms product, which is the finished platformate, passes through the stabilizer feed exchanger and is then water-cooled and sent to storage. The product, after the addition of tetra-



Two Single-Stage Compressors Recycle Hydrogen-Rich Gas Through Reactors
Combined capacity, 6,000,000 standard cubic feet per day



Heat Exchangers Located in Single Central Nest

Both fin-tube and G-fin types are used

ethyllead and inhibitor to prevent gum formation, is ready for direct use as motor fuel. The gum inhibitor is added largely as a safety measure since storage stability tests (17) show negligible gum formation on uninhibited platformate. Like the prefractionator, this column is heated by circulating bottoms which are heated by the product from the third reactor.

MECHANICAL EQUIPMENT AND DESIGN

The Old Dutch Platforming unit, although similar in over-all construction to other refinery equipment, presents special mechanical as well as process problems. The entire prefractionator section is constructed of carbon steel which is satisfactory for this type service. As in most crude oil distillation unit installations, there is some slight corrosion by the minute amount of alkyl chlorides which are formed in the acid treatment of oil wells. These compounds hydrolyze to acids wherever water condenses and attack the piping and vessels. The iron chlorides produced in such corrosion react with the hydrogen sulfide present to form iron sulfide. Corrosion in the prefractionator of the Platforming unit has been eliminated by the addition of ammonia to the top of the columns.

The greatest amount of special type equipment is found in the reactor section. The presence of high concentrations of hydrogen at high temperatures and pressures presents a material problem in this equipment. Hydrogen attack on carbon steel

becomes relatively rapid at temperatures above 500° F., but at temperatures below this level the attack drops to a rate which is so low that it can be neglected. In testing various steel alloys it has been found that alloys of the chromium-molybdenum type will withstand hydrogen attack at exceedingly high pressures and at temperatures up to levels at which the strength of the alloy is reduced. It is, of course, necessary to minimize the amount of these alloys used in order to keep the plant expense to a minimum. Where large vessels at high temperatures and pressures are required it is normally not economical to use alloy, both because of the difficulty encountered in the fabrication and because of the high cost. Alloy construction is avoided at Old Dutch by the use of internal insulation in the reactors to maintain the carbon steel walls at relatively low temperatures.

The reactors are cylindrical with conical bottoms. An upright steel cone surrounded by wire mesh is located at the bottom of the reactor to keep the ceramic balls supporting the catalyst from falling into the outlet pipe. Before charging the reactor with catalyst, a layer of porcelain balls graduated from 1-inch diameter at the bottom to $\frac{3}{8}$ -inch diameter at the top is placed in the bottom of the vessel. The catalyst itself is charged and then another layer of 1-inch balls to distribute the feed stream.

The high diffusivity of hydrogen which permits it to escape at high pressures, also pose a problem which must be carefully analyzed to avoid major losses of hydrogen. It has been found that

welding, unless carefully supervised and controlled, permits leaks which are not detected by ordinary methods but show up rapidly when exposed to hydrogen at high pressures and temperatures. It is also necessary to design carefully for hydrogen loss through flange joints and valve and pump packings. It is necessary to avoid materials which have any great degree of porosity, and where this is impossible it becomes necessary to design the stuffing box and glands for a breakdown of pressure in several stages with intermediate venting of the lost hydrogen to a low pressure point for return to the system.

INSTRUMENTATION

Instruments located on the control board are all of the transmission type, so that no hydrocarbon or hydrogen piping enters the control room. The instrument board is of the "graphic" type.

Temperature instruments are all electronic, including the indicating potentiometer. All heaters are temperature controlled. In spite of temperatures as high as 900° F., control valves on the effluent through reboilers and heat exchangers have given very little trouble. Constant differential pressure across the reboilers is secured by use of a differential pressure transmitter operating a controller to by-pass excess heating medium.

The differential pressure diaphragm-type flow transmitter has also been used for metering and flow control, in most cases with good results. Flow measurement of the recycle gas stream is made by an orifice by-pass type of rotameter. Pulsation

measurement errors have been minimized with this installation even though the meter is operating in the discharge line of two reciprocating compressors in parallel.

A set of sliding thermocouples connected to an eight-point recorder is installed in the reactors to permit exploration of catalyst bed temperature. The data obtained from these thermocouples is not vital to efficient operation of the unit, but it is expected to be of value in the engineering design of future units.

TABLE VII. PERFORMANCE DATA—OLD DUTCH PLATFORMING UNIT, PERIOD FEBRUARY 6 TO 9, 1950

Hours on catalyst	1961-2057		
Av. reactor pressure, lb./sq. inch gage	720		
Av. reactor temp., ° F.	890		
Observed rates and yields, vol. % of charge			
Reactor charge	100		
Stabilized platformate	92.6		
Calcd. 10-lb. vapor pressure platformate			
Yield	97.1		
Outside butane required	4.5		
	Reactor Charge	Stabilized Platformate	Calcd. 10-Lb. Vapor Pressure Platformate
Inspection			
Paraffins, %	62	61	...
Olefins, %	0	1	...
Naphthenes, %	33	1	...
Aromatics, %	5	37	...
Sp. gr., ° API	58.1	57.4	59.7
Vapor pressure at 100° F. (5)	2.0	6.9	10.0
Sulfur, %	0.08 (Lamp)	0.0019 (Turbidimetric)	...
Octane No.			
Research			
Clear	52.5	81.3	81.9
Plus 3 cc. TEL	70.2	93.9	94.7
Motor			
Clear	48.9	75.5	76.1
Plus 3 cc. TEL	68.5	87.4	88.2
A.S.T.M. distillation			
Initial boiling point	166	110	...
10	203	155	...
30	225	195	...
50	248	225	...
70	273	260	...
90	309	308	...
End point	355	363	...
Component yields			
Standard cu. ft./bbl.			
H ₂	...	401	...
C ₁	...	80	...
C ₂	...	53	...
C ₃	...	65	...
Volume %			
i-C ₄	...	2.1	...
n-C ₄	...	3.5	...
i-C ₅	...	5.0	...
n-C ₅	...	2.9	...
C ₆ +	...	80.2	...



Three Adiabatic Reactors in Series Complete the Reforming of Naphtha Charge

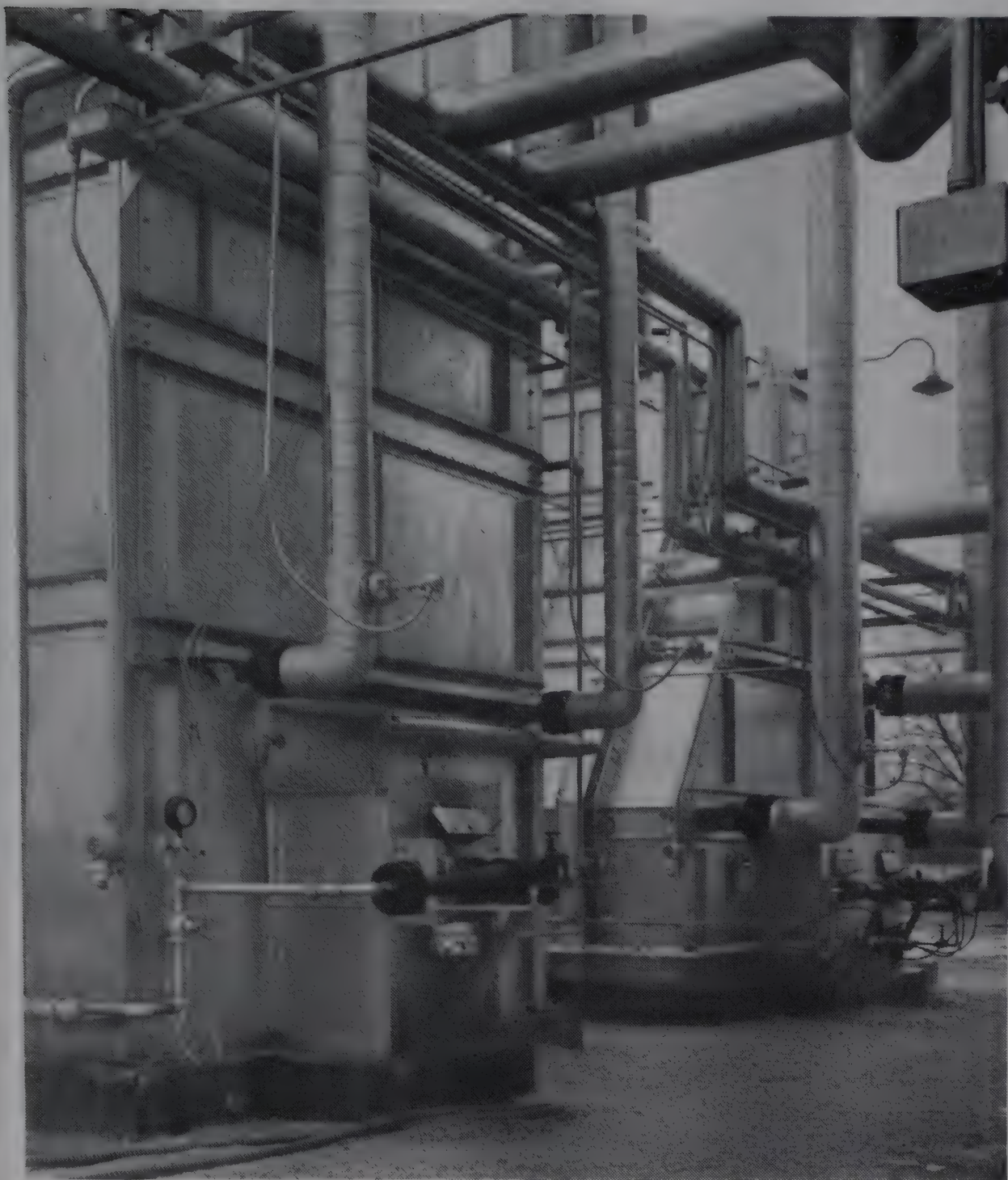
Distribution towers for feed preparation and product stabilization are in background

AUXILIARY EQUIPMENT

All pumps in the unit, except the main feed pump, are the centrifugal type with cast-iron impellers. In the Old Dutch unit this is a duplex plunger-type, motor-driven through a hydraulic drive and a speed reducer (2A). In a larger plant it might be a multistage centrifugal pump.

The recycle gas is compressed by two single-stage piston-type compressors with a combined capacity of 6,000,000 standard cubic feet per day (1A). These are motor-driven and non-lubricated—that is, they have carbon piston rings. All valves used in the plant are standard types; gate valves are used for cutoffs and globe types for check or throttle service.

Conventional spring-loaded pressure relief valves are located throughout the unit according to the code of the American Society of Mechanical Engineers (1). Those on gas lines are connected to a burning pit, some distance away from the unit, where a continuously burning torch ignites the escaping gases. Relief valves which will discharge a liquid stream are vented to an oil sump connected to the waste disposal system provided for the other units in the plant.



Reactor Interheater and Recycle Gas Heater

Both are fired with excess gas produced by the platforming process; interheater (background) has two independent sets of coils of different size to heat the reaction stream between the first and second, and third and fourth reactors

The Platforming unit itself requires no waste disposal since its only waste product is a gas which can be burned under the furnaces without scrubbing or other treatment. The only water required by the unit is that used in cooling coils. The discharge from those coils is cooled in a cooling tower and recirculated. Make-up water is obtained from the municipal water system of Muskegon.

ANALYTICAL CONTROL

The laboratory data that must be accumulated to control the Platforming consists primarily of check tests, by laboratory distillation, on the prefractionator and reactor charge and on the stabilizer bottoms product. These distillations assure the operator that the fractionating columns are operating to provide a satisfactory feed and produce a satisfactory product. Additional check distillations are occasionally made and the prefractionator overhead and bottoms are inspected, as well as the stabilizer reflux sample.

Changes in the type of charge stock due to changes in crude oil require that octane numbers, both clear and leaded, as well as sulfur content and distillation range be determined. These analyses are made on the prefractionator charge tank when the crude distillation unit operations indicate it is necessary. Total sulfur content of both the charge and product is determined by turbidimetric or titrimetric tests, the latter being applied when the sulfur content is exceptionally high.

The hydrogen content of the recycle gas is determined by a continuous meter activated by the selective diffusion of hydrogen through a palladium tube installed directly in the gas line (36). The analyzer reads directly in partial pressure of hydrogen; the reading is transmitted pneumatically to a remote location.

The recycle gas is analyzed occasionally for hydrogen sulfide by the Tutweiler method (4) when very high sulfur stock is being run.

The final product as it comes from the bottom of the stabilizer is tested for distillation characteristics, specific gravity, Reid vapor pressure, sulfur, and mercaptans by the doctor test using sodium plumbite; corrosion by copper strip test; and octane numbers by research and motor method both clear and leaded. It is also checked for gum stability by oxygen bomb and copper dish tests.

PERFORMANCE OF THE OLD DUTCH PLANT

The success of the platforming process is due to the development of a catalyst which will promote the desired reactions while suppressing carbon formation. The favorable octane-yield characteristics of the process indicate the efficacy of the catalyst and pilot plant runs indicate a very low rate of carbon deposit on the catalyst. Operations at Old Dutch for 4 months have resulted in no measurable decrease in catalyst activity. In early operation the iron sulfide product of the corrosion mentioned earlier was carried over to the No. 1 reactor. The dust was filtered out by the porcelain balls above the catalyst as a dense powdery layer. The increase in pressure drop through the reactor caused by this layer necessitated the shutdown of the plant in early January. The deposit was easily removed by screening and the catalyst was found at that time to be essentially unchanged from its original physical and chemical state. Ammonia gas is now being introduced into the prefractionator to neutralize the feed. Water added to the overhead discharge line dissolves out the ammonia salts formed. The resultant liquor is taken off at the reflux drum with the feed moisture. The only other shutdowns which have occurred have been necessitated by leaking of pressure relief valves.

The Old Dutch unit was designed to produce a product with a leaded research octane number of 89 to 90. However, during the period of construction, the octane number demanded in Old Dutch's marketing area increased substantially. As a result, the unit has been operated to produce gasoline with a leaded octane value of 93 (Table VII). Yields under these conditions have averaged 94.5% by volume. The unit was operated for a period of several weeks to produce a product having a leaded octane number of 95.8 with a yield of 92 volume %.

Total gas production amounts to about 400,000 cubic feet per day of which more than one half is taken from the separator and contains 80 to 85% hydrogen. The remaining gas is taken from the stabilizer overhead.

PLATFORMING OF STRAIGHT-RUN AND CRACKED GASOLINE

Although the Old Dutch Platforming unit is constructed to run on straight-run naphtha, some future plants will be designed to charge a mixture of straight-run and cracked gasolines. Such units are expected to produce a product very similar in quality to that produced from straight-run stocks alone, although the feed will have a much higher olefin content. Inasmuch as the fraction of thermally cracked gasoline boiling below about 200° F. is an already good fuel from the standpoint of octane number, only the higher boiling fraction of thermally cracked gasoline would be included in the charge to the platformer.

Since olefin containing stocks usually cannot produce as much hydrogen as straight-run gasolines, cracked gasoline generally is not Platformed alone but is mixed with straight-run naphtha to maintain a high hydrogen concentration in the recycle gas.

CAPITAL AND OPERATING COSTS

The operating cost of a Platformer having a capacity of 1500 to 2000 barrels per stream day is shown in Table VIII. The figures shown are believed to be conservative. The value given for utilities does not include the fuel gas because the Platforming process produces an excess of such gas except at very low severities of operation.

TABLE VIII. OPERATING COSTS FOR PLATFORMING STREAM DAY CHARGE OF 1500-2000 BARRELS

	Cost per Barrel of Reactor Charge
Operator and part-time helper per shift	\$0.04-0.05
Royalty (present rate)	0.07
Catalyst	<0.10
Maintenance	0.03-0.05
Taxes and insurance	0.04-0.05
Utilities	0.04-0.05
Total	\$0.30-0.37

TABLE IX. APPROXIMATE UTILITY REQUIREMENTS FOR 1500-BARREL PER DAY PLATFORMING UNIT

Steam, lb./hr.		
Pumps (125 lb.)	650	800
Process (15 lb.)
Cooling water (85° F., and 75 lb./sq. inch), gal./min.	700	900
Electricity (440 volts, 3 phase, 60 cycles), kw.-hr.		
Power: pumps and compressors	205	250
Lights	15	25
Process
Total	220	275
Air (for instruments only), standard cu. ft./min.	35	45
Fuel gas for all heaters (1290 B.t.u./cu. ft., 16.6 av. mol. wt.), cu. ft./hr.	19,250	25,100

At average labor costs in the mid-continent area and with all new equipment, the installation cost of platforming units range from about \$700,000 for a 1500-barrel-per-stream-day charge to reactors to \$1,600,000 for a 5000-barrel-per-stream-day charge and \$2,500,000 for a charge of 10,000 barrels per stream day. Utility requirements for a 1500 barrel-per-day plant are given in Table IX.

PERFORMANCE OF PLATFORMATE

The product of the Platforming process has a boiling end point slightly above that of the charge but not enough to require re-distillation. Platforming can be used to produce gasolines with octane ratings up to 100, with reasonable loss of yield, but most plants will probably be run to give a product with a rating of about 93. However, the antiknock performance measured by the so-called road octane rating for this product ap-

proaches 100. Although some disagreement between research and road ratings is customary, a spread of this magnitude is quite unusual.

ACKNOWLEDGMENT

The data on operating variables used in this article were obtained from pilot plant operations conducted at Riverside, Ill., under the supervision of the inventor of the process, Vladimir Haensel of Universal Oil Products Company, and are presented with his kind permission (17). The authors also wish to acknowledge the valued assistance of the management and engineering staffs of the Old Dutch Refining Company in the preparation of this article.

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PROCESSING EQUIPMENT

- (1A) Chicago Pneumatic Tool Co., Chicago, Ill., Type TEO 6 × 13 6,000,000 standard cubic feet/day motor-driven compressor.
- (2A) Oil Well Supply Co., Wilson-Snyder Mfg. Div., Braddock, Pa., 3 1/2 × 12 inch duplex plunger pump.



Liquid Fuels from Oil Shale

Refinery, N-T-U Retorts, Storage Bins, and Crushing Plant (left to right) at U. S. Bureau of Mines Oil-Shale Demonstration Plant, Rifle, Colo.

WILLIAM Q. HULL

Associate Editor

in collaboration with

BOYD GUTHRIE AND E. M. SIPPRELLE

U. S. Bureau of Mines, Rifle, Colo.

THE distillation of "an oyle from some kind of stone" was described in a British patent (6) in 1694. The reference is presumably to shale and is believed to be the first recorded interest in the subject (3). Even earlier, in the middle of the 14th century, the term "petroleum" was used in England in referring to oils derived from rocks (10). Thus, long before the beginning of our modern industry founded on flow oil, "petroleum" was applied to shale and similar rock oils, and since the term is derived from the Latin *petra* or rock, and *oleum* or oil, its earlier application was literally correct. However, the term has long been associated with that mixture of hydrocarbons derived in a liquid form from wells drilled into the earth's surface. Oils derived from naturally occurring solid formations are included today in the field of synthetic liquid fuels.

The United States, endowed with abundant supplies of naturally occurring gas and petroleum, also has extensive deposits of oil shale, coal, and other starting materials for the preparation of synthetic fuels. Although early American use of synthetic oil dates back as early as 1855 when the Mormons retorted oil shale in Utah (1), interest in the development of a synthetic fuel industry has been characterized by revivals and subsidences beginning with the discovery of petroleum in Pennsylvania in 1859. The fluctuating interest was a result of the phenomenal increase in petroleum usage and growth of the petroleum industry and the ever changing and conflicting opinions of the extent of our unused petroleum reserves. During the decade beginning with 1850, more than fifty plants were erected in the states along the Atlantic Coast to retort imported Boghead coal and local coals and shales, as well as plants to treat the Albert Mines shale in Canada. How-

ever, with the discovery of large American petroleum fields, the enterprises failed to survive the resulting competition, and the distillation plants were compelled to close. Later some were remodeled into refineries for well petroleum. The processing of coal and shale into synthetic liquid fuels then became a subject merely of academic interest.

The annual per capita use of oil in the United States has increased from 4 to 14 barrels in the last 30 years. Natural gas consumption shows a similar startling growth from 7500 to 35,000 cubic feet since 1920. During the same period, coal consumption dropped from 6 to 4.5 tons per person. However, the energy derived from coal in 1948 was approximately the same as in 1920. The trend toward greater usage of oil and gas, the reserves of which have limitations, has resulted in a change from the former academic interest in synthetic fuels to thorough investigations of the feasibility of the development of a synthetic fuels industry.

The United States Government first became seriously concerned in the production of liquid fuels from shale and coal shortly after World War I, when a growing interest in the importance of liquid motor fuels was in evidence. In 1925, the Bureau of Mines constructed an oil-shale experiment plant near Rifle, Colo., where fundamental work in the mining and retorting of Colorado shale was conducted until 1929, when the plant was closed following the discovery of large oil fields in California, Oklahoma, and Texas, and an abundance, rather than a scarcity, of petroleum was indicated. During World War II, when the United States faced the possibility of a serious petroleum shortage, plans were made for the Bureau of Mines to conduct comprehensive studies of the technical and economic problems in-

volved in the production of synthetic fuels. In 1944, Congress passed the Synthetic Liquid Fuels Act (18), authorizing the expenditure of \$30,000,000 over a 5-year period, to construct and operate demonstration plants to produce synthetic liquid fuels from coal, oil shales, agricultural and forestry products, and other substances. The act further authorized the Secretary of the Interior, acting through the Bureau of Mines, to carry out the provisions of the act. Two extensions to the act have authorized the expenditure of \$87,600,000 over a total period of 11 years and increased its scope to include work on secondary recovery of petroleum. The Bureau of Mines delegated the responsibilities for work on agricultural and forestry products to the Department of Agriculture and work on secondary recovery to the Petroleum and Natural Gas Branch of the Fuels and Explosives Division of the Bureau of Mines. The Office of Synthetic Liquid Fuels was created as a branch of the fuels and explosives division to carry out the research and demonstration plant work on the production of synthetic liquid fuels from coal and oil shale.

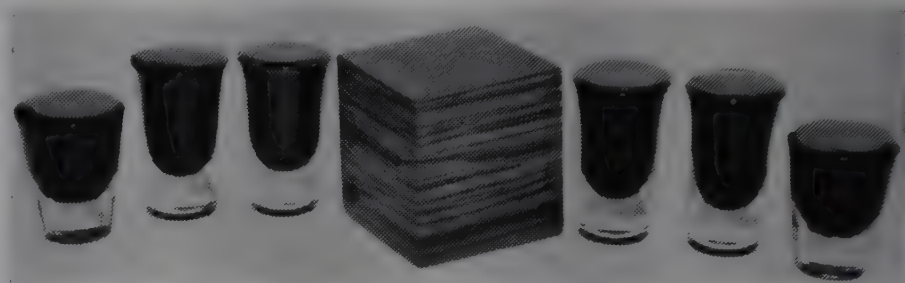
The United States Department of Agriculture is conducting research and developing methods for the production of alcohol and other liquid fuels from agricultural residues including corn cobs and hulls of cottonseed, oats, and rice. A liquid fuels plant was constructed in 1946 on the site of the Northern Research Laboratories at Peoria, Ill., in order that the programs of the two groups might be coordinated. Studies of the fermentation of pentose and dextrose sugars to liquid fuels are being made, and the various fuels produced are undergoing extensive testing.

The secondary recovery phase of the program deals with stripper oil fields and refining processes. Bureau of Mines field headquarters, acting as centers of activities on secondary recovery research, include Bartlesville, Okla., Laramie, Wyo., San Francisco, Calif., Dallas, Tex., and Franklin, Pa. Measurable technical progress has been made to lessen the quantity of oil previously classed as unrecoverable in stripper fields and to improve the utilization potentialities of the so-called marginal crudes, especially those with a high sulfur content.

The Office of Synthetic Liquid Fuels established research laboratories at Bruceton, Pa., Morgantown, W. Va., and Laramie, Wyo., and demonstration projects at Louisiana, Mo., and Rifle, Colo. The Bruceton laboratory carries on research work in connection with coal hydrogenation; the Morgantown laboratory devotes its efforts to synthesis gas production from coal; and the laboratory at Laramie works on research problems concerned with oil shale and shale oil (14-16). The demonstration project at Louisiana, Mo., works on coal and in reality consists of two demonstration plants employing two basically different processes for converting coal to liquid products; the direct hydrogenation or Burgess process and the gas synthesis or modified Fischer-

Tropsch process. The direct hydrogenation plant was dedicated May 7, 1949, and has been described in detail (7). The gas synthesis demonstration plant is scheduled to be in operation in 1950. The oil-shale demonstration project at Rifle is divided into two major phases: one dealing with mining of the oil shale and the other with the extraction of the oil from the shale and refining of shale oil into liquid fuels (Figure 2).

Research and demonstration activities are closely coordinated, with the research laboratories working in the main to obtain basic research data and to develop processing techniques on a bench scale size, whereas the demonstration plants design, construct, and operate pilot plant processing units to obtain the required process and engineering data which are used to build and operate demonstration scale units of sufficient size that accurate designs and cost information can be projected to commercial size installations.



A 3-Inch Cube of Oil Shale Yields 6 Fluid Ounces of Shale Oil by Gas-Flow Process

Shale assays 38 gallons per ton by modified Fischer assay method

Some 150 cooperative agreements with industry, universities, research institutions, and the armed services on oil shale and shale-oil processing are in existence. These agreements in the main provide for furnishing raw materials for testing to the co-operators, and in return the Bureau of Mines is furnished the information resulting from these investigations. The bureau reviews and coordinates these results and disseminates the information obtained therefrom, with consent of the co-operators, to augment the general knowledge of the subject of oil shale. This article describes the work of the Bureau of Mines and work under a few cooperative agreements with private investigators on the recovery of liquid fuels from oil shale.

OIL SHALE AND HISTORY OF SHALE-OIL RECOVERY

Oil shale has been defined by the American Society for Testing Materials (2) as: A compact rock of sedimentary origin, with ash content of more than 33% and containing organic matter that yields oil when destructively distilled but not appreciably when extracted with the ordinary solvents for petroleum.

A large variety of rocklike materials occurring throughout the world and known by various names including oil shale, torbanite, kukersite, and others have the common characteristic of containing the large proportion of carbonaceous oil-yielding material, as specified in the A.S.T.M. definition, but have other characteristics that differentiate them. However, oil-soaked sands such as are found in California, Utah, and Alberta, Can., are not oil shales because the oil can be extracted by organic solvents. True oil

TABLE I. SUMMARY OF DIRECT MINING COSTS PER TON OF SHALE

	(Top heading and middle bench test run)							
	Operating Labor	Maintenance Labor and Parts	Power	Fuel	Explosives	Bits and Drill Rod	Other	Total
Drilling ^a	\$0.018	\$0.004	\$0.004	\$0.001	..	\$0.020	..	\$0.047
Blasting ^a	0.010	\$0.072	..	\$0.002	0.084
Loading ^b	0.018	0.014	0.003	0.002	0.037
Transportation ^b	0.023	0.024	..	0.004	0.051
Scaling	0.017	0.001	0.018
Foreman and surveying	0.013	0.013
Electrical distribution	0.016	0.016
Miscellaneous	0.001	..	0.002	0.004	0.007
Labor burden ^c	0.019	0.019
Total	\$0.100	\$0.043	\$0.009	\$0.007	\$0.072	\$0.020	\$0.041	\$0.292

^a Maintenance costs on these units are based on calculated cost of continuous operation at the oil-shale mine for 1 year.

^b Maintenance costs on these units are based on the per hour cost of maintenance parts and maintenance labor as supplied by the manufacturers of the units.

^c Labor burden based on actual operating and maintenance labor charged during the test run. Disposition is based on 260 working days: annual leave, 10.0%; holidays (8 days leave with pay), 3.1%; sick leave, 4.0%; total, 17.1%.

shale is a fine-grained sedimentary rock with a laminar structure quite similar to slate. It varies in color from gray or bluish gray or brown or reddish brown to almost black, and there is little outward appearance or feel of oiliness. However, rich, thin pieces can be ignited with a match and will burn with a sooty flame and



Underground Quarry

Electric shovel loading dump truck on bench level; bench-level drilling operation (upper right); portable compressor and utility unit (upper left)

petroleumlike odor. The shale contains up to 25% of a solid organic material known as "kerogen" which was derived by combining two Greek words meaning "producer of wax."

Kerogen is a complex organic mixture and not a definite chemical compound; and the kerogen content of different shales varies considerably (16). The kerogens have the common property of reacting to form a liquid hydrocarbon oil on distillation of the rock. Oil vapors appear at temperatures of 482° to 662° F., and all kerogen is converted if the temperature is increased to 842° to 1022° F.

Oil shale is distributed in many parts of the world; the composition, properties, and oil yields of deposits vary widely as shown in Tables I, II, and III of Thorne *et al.* (16) in which Colorado shale is compared with several foreign shales.

France is credited with having developed the first commercial exploitation of oil shale. Using the process patented by Selligie (13), in which superheated steam is the source of heat for retorting, a French shale-oil industry had its birth in 1839 and expanded to about 1865, when the lower cost of imported American products threatened the industry. However, subsequent tariff protection has permitted its survival to the present day. Following shortly after the beginning of the industry in France, commercial shale oil extraction was started in Scotland; the first establishment treating shale exclusively in Broxburn in 1859. James Young (1811-83) developed an intermittent horizontal type retort in which oil shale was dry distilled at a low temperature, and shortly after in 1860 the forerunners of the vertical type retort, in use today, made their appearance. Twelve mines are in operation at the present time and supply shale to five crude oil works producing crude oil, naphtha, and ammonium sulfate. The crude oil and naphtha are processed to marketable products

at the Pumpherston refinery. Additional commercial oil-shale industries exist today in Australia, Manchuria, Estonia, and Sweden.

DEMONSTRATION PLANT

The Bureau of Mines experimental oil-shale mine and demonstration plant are located on Naval Oil-Shale Reserves 1 and 3 at Anvil Points, about 10 miles west of Rifle, Colo. The mine is at an altitude of 8200 feet and overlooks the plant site 3000 feet below; these are connected by a 5.5-mile winding, mountain road. The mined shale is hauled in Diesel trucks to the crushing plant. From here the shale is available for retorting and the crude oil for storage and eventual refining.

The oil-shale mine is in the Parachute member of the Green River formation, which extends through western Colorado into Utah and Wyoming. The main oil-shale measure is near the top of the Green River formation and averages 500 feet in thickness. The shale yields approximately 15 gallons or 0.36 barrel of shale oil per ton. The lower horizon of the 500-foot measure, called the Mahogany ledge, varies from 50 to 100 feet in thickness and averages a yield of approximately 30 gallons or 0.7 barrel per ton. The oil-shale measure outcrops in bold cliffs for a distance of 145 miles in the area, and sampling of outcrops and core drilling indicate the oil-shale measure in the surrounding 1000-square mile area contains 300 billion barrels of shale oil. The Mahogany ledge alone, which appears most practical for the first commercial exploitation, represents 100 billion barrels.

Mining

Low cost mining of oil shale was the first problem to be solved in order that a commercial industry might receive practical consideration. The experimental mine has adopted surface mining practices to a great degree, since mining costs are considerably lower in quarries and open-cut mines; the operating mine is referred to as the "underground quarry."

In the actual mining operation, entries are driven into the oil shale from the outcrop of the Mahogany ledge. The mine is laid out with 60-foot-square pillars to support the overlying formation, and the pillars are spaced 60 feet apart in both directions and staggered in one direction, as shown in Figure 1. A loosely cemented bedding plane exists at the top of the Mahogany ledge, and the rock above this parting is a low grade marlstone of sufficient strength to serve as a roof stone without any timbering or roof supports whatsoever. A test room 80 feet wide and 100 feet long stands unsupported, and from accurate microseismic noise level readings and roof and floor convergence measurements there has been no indication of failure of the roof stone to date. The

TABLE II. PRODUCTION

(Top heading and middle bench test run)

Tons mined in 20 shifts		32,560
Labor		
Tons per 8-hour man-shift (underground labor)	148.2	
Tons per 8-hour man-shift (total labor force, including direct supervision engineering and all maintenance)	116.1	
Labor percentage of total direct cost	43.8	
Power and supply items		
Power, kw.-hr. per ton		0.708
Drilling	0.321	
Loading	0.223	
Utilities	0.164	
Tons broken per pound of explosive		2.54
Tons broken per foot of drill hole		1.986
Feet of drill hole per drill bit		1171
Feet of drill hole per drill rod used		513
Tons of oil shale transported per gallon of fuel used		27.66
Gallons of water per ton		1.75
Drilling	0.577	
Wetting broken oil shale	0.775	
Spraying road	0.398	

room is currently being lengthened to 200 feet and will be widened to 90 feet in the near future.

Advance top-level headings 60 feet wide by 27 feet high are first driven immediately under the roof stone by means of horizontal blast hole drilling and blasting. In a commercial operation, the remaining shale would be mined by following the advance headings with 22-foot benches similar to quarry operations. In the experimental mine, one bench is mined, since it is considered that costs and techniques established on the middle level will be the same as in the third level.

A goal of a minimum of 100 tons per man-shift was set up. It was established that standard equipment would be adequate for loading and transporting the broken oil shale, but it was evident that conventional drilling and blasting practices would have to be modified in order that the required tonnage per man-shift might be realized. A unique heading jumbo was developed for drilling horizontal blast holes. The unit consists of two platforms mounted on a framework at the rear of a Diesel truck. Each platform has two 4-inch percussion drills mounted on 16-foot feed slides. The vertical inclinations of the feed slides are controlled by screws and ratchets; air hoists are used for raising and lowering the platforms; and spur gear devices permit swinging the platforms to various horizontal angles. A water tank and air hoist are mounted on the truck. Preparatory to drilling, it is only necessary to connect a 3-inch air hose. The four drills mounted on the carriage are operated by two men. By use of the multiple-drill carriage, two miners drill out a round comprising seventy-two 15-foot holes in less than 6 hours, breaking nearly 1700 tons of shale.

A second drilling rig has been developed for drilling vertical holes on benches. Similar to the heading carriage, it mounts four 16-foot drill feeds, each carrying a 4-inch percussion drill. A Diesel tractor forms a mobile base for the rig. The carriage is operated by two men who drill a bench round consisting of forty-eight 22-foot holes in approximately 7.5 hours. Each vertical drill round breaks approximately 3400 tons of shale.

The horizontal blast holes, 25 feet above the floor in the top headings, required the development of a special piece of equipment for charging. The unit consists of a 5 × 10 foot wooden platform mounted on a fork-lift truck. The truck, powered by a Diesel engine, has a power hoist for raising and lowering the platform from which the powdermen charge the explosive into the blast holes. A charge of 680 pounds of 45% semigelatin dynamite in 1 $\frac{7}{8}$ × 12 inch cartridges is required to blast a top level heading round.

A standard 2.5-yard electric shovel with a short boom to permit working under a 25-foot height is used for loading the broken shale. Since shale is relatively light in weight, averaging 15 cubic feet to the ton, the 2.5-yard dipper was replaced with one of 3-cubic yard capacity. The shovel handles as much as 300 tons of shale per hour. Three 15-ton Diesel end-dump trucks are used for transporting the shale, which is loaded directly into the trucks by the shovel. A caterpillar bulldozer is used for cleanup work during the loading operations.

Water for wetting down the broken piles of stone and for spraying the roadways is supplied from a water truck with a 700-gallon tank and a high pressure pump. Drilling water is also supplied by this truck. After each blast loose rock must be scaled from the heading face. The roof and the pillars in other parts of the active mine workings are also inspected and scaled periodically. Another special unit of equipment has been developed for this purpose. It consists of a telescopic mast mounted on a fork-lift truck. With the tower fully extended, the platform is 65 feet above the mine floor, and the scaling rig can be used on any level of the oil-shale mine. Two men working on the platform pry loose rock from the roof and upper parts of pillars by means of aluminum rods with steel tips. A small percussion drill is used for drilling loose slabs of rock not easily removed.

An early study showed that the cost of laying and moving air and water lines on the advancing levels of the underground quarry would be a considerable item of expense; air and water lines would interfere with other work; and pressure losses would reduce drilling speed with pneumatic drills. To overcome these difficulties, a movable compressor assembly was designed. The

utility station is constructed on a 30-ton trailer, 30 feet long and 12 feet wide. It is equipped with steering dollies at both ends and may be towed from either. The trailer carries two 770-cubic foot-per-minute compressors, a 2500-gallon water tank, and a 200-cubic foot air receiver. The compressors are driven by two 150 hp., 2300-volt electric motors. The assembly is operated by the mine mechanic who also maintains other mining equipment underground. Water used in the mine is supplied through a diamond drill hole from a 10,000-gallon tank located on a plateau

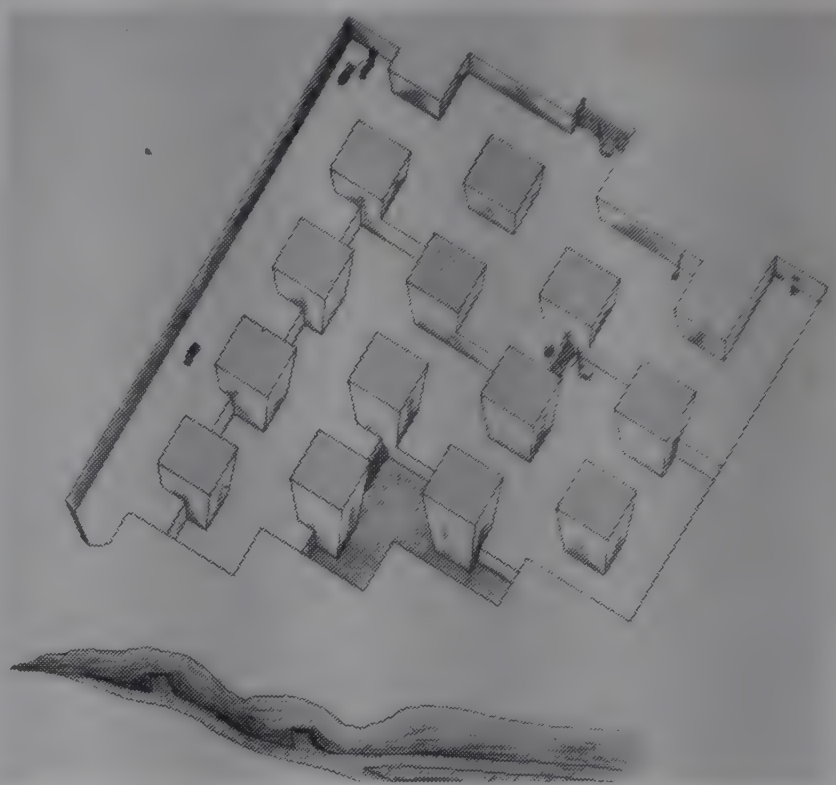


Figure 1. Method of Mining Developed in Bureau of Mines Underground Quarry

above the cliffs in which the mine is located. Two earthen dams, capable of impounding 700,000 gallons of water, have been constructed on the plateau. Water for the housing area and plant is taken from the nearby Colorado River.

Production Test Run

In the autumn of 1949, a production test run was conducted utilizing the mining practices that had been developed and the equipment that has been described. During this test run, the top level was mined for 2 weeks and a bench level for the following 2 weeks, since sufficient equipment was not available to operate both levels concurrently. The operational procedures during the test run were identical to those that would be employed in one unit of a commercial mine, but do not necessarily represent the optimum results that ultimately may be obtained. The top-level mining crew consisted of a total of thirteen men, including one shovel operator, one bulldozer operator, three truck drivers, two drillers, two blasters, two scalers, one mechanic, and one foreman. A labor crew of eleven men worked the bench level. Tables I and II show summaries of costs and production during the test run.

Mining Research

An extensive research program is being conducted at the oil-shale mine to obtain solutions to several significant problems, all of which will contribute to further lowering of mining costs and improvements in mining techniques. At the present time, efforts are being concentrated in four fields:

1. Development of a successful rotary drill
2. Improvement in blasting technique
3. Development of more efficient underground loading equipment
4. Further study of roof and pillar stresses

MINING AND PROCESSING OPERATIONS



PLANT PROCESS SERIES

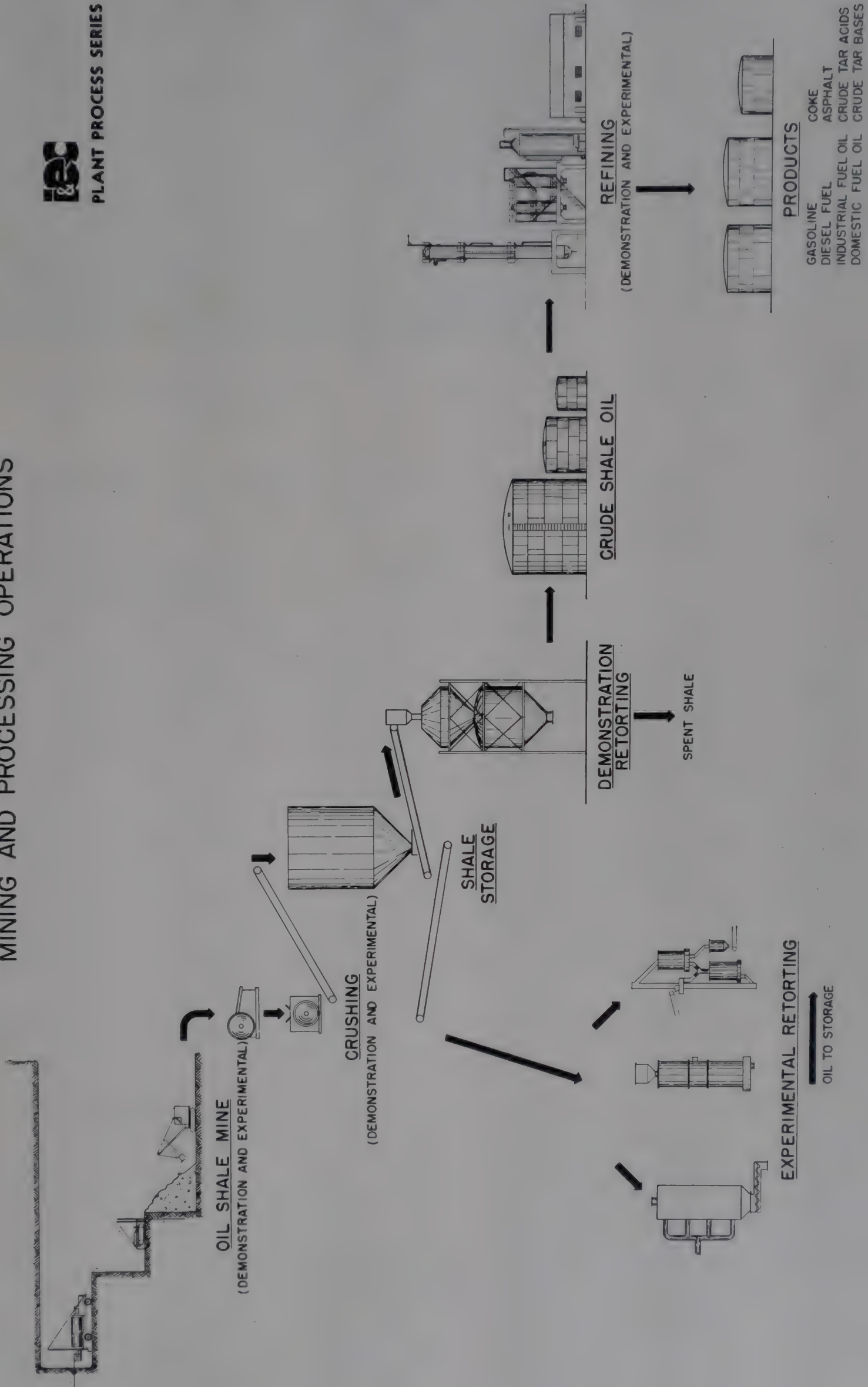


Figure 2. Flow Sheet of Mining and Processing Oil Shale at U. S. Bureau of Mines Experimental Oil-Shale Mine and Demonstration Plant, Rifle, Colo.

Crushing

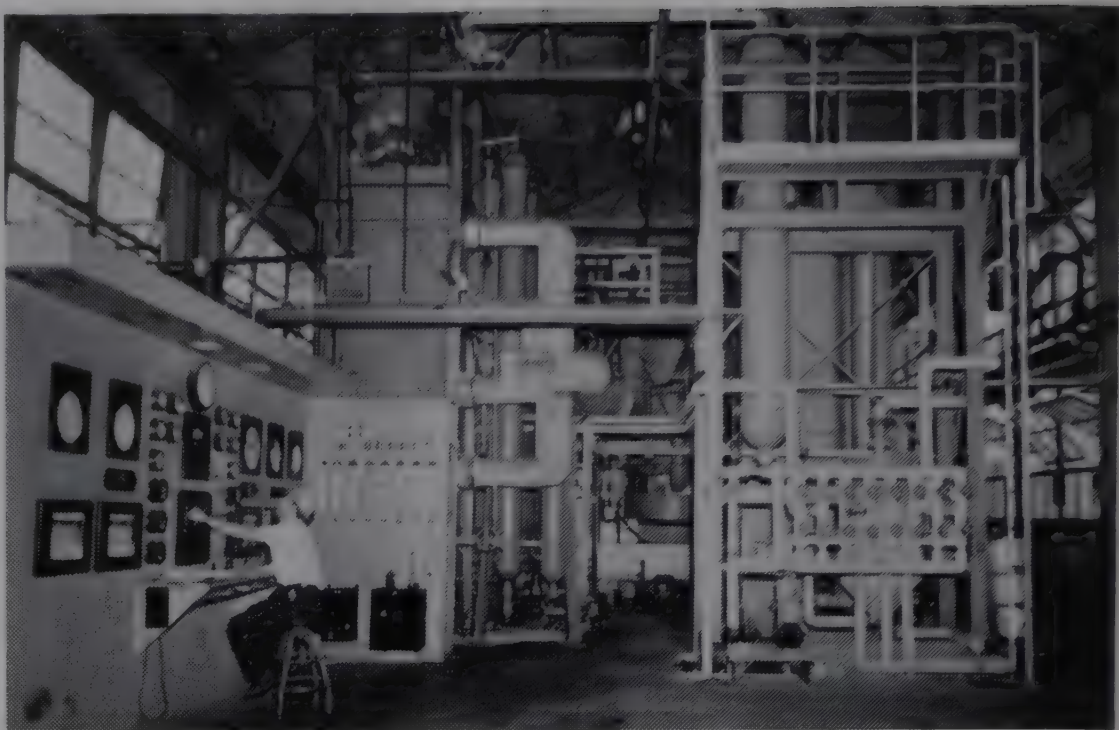
The first step in the preparation of the oil shale from the mine is the reduction of the shale to proper size for various retorting processes. Retorting requirements dictated that the crushing plant be able to crush all existing grades of shale from lean to rich and to produce a crushed shale of 6-inch maximum size at a rate of 30 to 60 tons per hour. The shale resulting from blasting in the mine ranges in size from dust to 75 inches, the larger pieces being of cubical or flat-slab form. A maximum particle size of $24 \times 24 \times 18$ inches was established for the crushing plant and over-size pieces are broken to this size before delivery to the plant. The maximum crushing plant output is 80 tons per hour, depending on the grade and particle size range of the crushed oil shale produced. The nature of retorting characteristics indicates that a crushed shale as near cubical in form as possible, with minimum fines, is desirable.

The crushing plant includes primary, secondary, and tertiary crushers. Ore is unloaded from mine trucks directly into a receiver hopper. An apron feeder carries the shale from the hopper to the primary crusher, which is a double-toggle type jaw crusher with 36×42 inches intake. The jaw crusher opening can be varied from 4 to 6 inches giving product sizes within these ranges including approximately 15% oversize above maximum opening. The capacity is 100 tons per hour. Belt conveyers transfer the crushed shale to a two-decked vibrating screener above the secondary crusher. The particle size range desired in the crushed product is obtained by using screens of the proper mesh on the upper and lower decks. The fines passing through both screens go to a belt conveyor below and are discharged to a stock pile to await future retorting studies or to be used for grading and surfacing of roads in the plant area. Material passing through the upper screen and retained on the lower screen is conveyed to one of three 150-ton storage bins. The material retained on the upper screen is conveyed to the secondary crusher, which is a Blake-type, all-steel, single-toggle, roller-bearing jaw crusher. The intake is 10×30 inches and jaw swing is 0.5 inch with closed jaw opening ranging from 1 to 6 inches. The capacity is 15 to 30 tons per hour. The discharge from the secondary crusher is returned to the head of the vibrating screens by a bucket conveyor and recycled through the screening operation.

A tertiary crusher is provided to supply extra-fine shale for experimental pilot plant retorting operations. It is a gearless, low-head gyratory crusher with maximum receiving opening of 3 inches and delivers 20 tons of minus 4-mesh crushed shale per hour.

Retorting

When oil shale is destructively distilled, the evolution of oil from the kerogen takes place in two stages (11). A primary decomposition occurs, in which the insoluble kerogen changes into a soluble solid, or semisolid, bitumen. The intermediate bitumen is unstable and a secondary decomposition changes it into lighter oils of greater stability and higher saturation. The characteristics of oils recovered from different shale deposits vary greatly. Like petroleum, they may be classified as of paraffinic, asphaltic, or mixed base. The oils from Scottish and Tasmanian shales are of paraffinic base; oils from Nevada shales are of paraffinic base, from Kentucky of asphaltic base, and from Colorado and Utah, intermediate. The yields of oil from various oil shales and from various locations and strata of the same deposit may vary greatly. Some of the properties have very definite effects on retorting, and these must be considered in the design of



Pilot Plant Gas-Flow Retorting Process

Retorting vessel is at left beyond instrument panel; tubular condensing equipment at right

the retorting equipment (16). One property which varies widely among different shales is the tendency of a shale to agglomerate when heated. The differences in the mineral carbonate and organic composition of the kerogen are at least partly responsible for this phenomenon. This coking and clinkering tendency predominates in Green River shales assaying more than 30 gallons of oil per ton but is of minor consideration in retorting some shales, such as Swedish alum shales. Unless the temperatures are controlled accurately during retorting, shales having a pronounced coking tendency will produce oil-free shale residues that will clog the discharge mechanisms of a continuous retort. The presence of relatively large percentages of mineral carbonates in

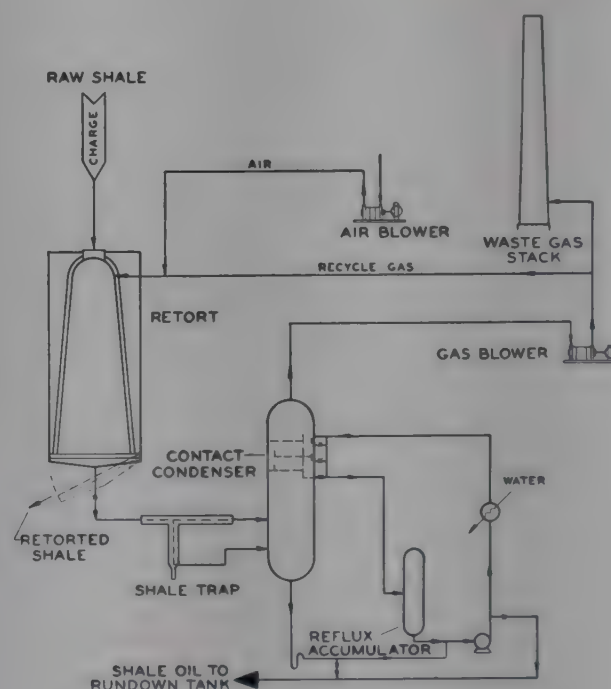


Figure 3. Flow Diagram of N-T-U Retorting and Condensing System

oil shale limits the heat efficiency of those retorting processes in which the shale is heated to temperatures sufficiently high for carbonate decomposition. This decomposition occurs at elevated temperatures yielding carbon dioxide amounting to about 20% of the weight of the raw shale. Since the decompositions are endothermic and it is highly desirable that the heat for retorting be supplied from a portion of the retort products, such as gas or fixed carbon on the spent shale, delicate control of retorting temperatures is necessary.

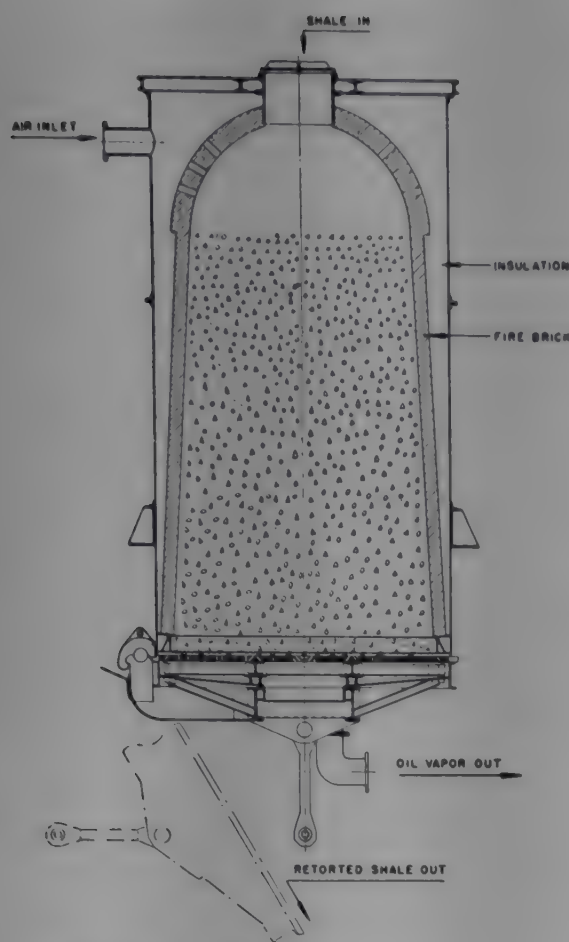


Figure 4. Sectional View of N-T-U Retort Vessel

Although hundreds of retorts have been designed and patented, they may be divided into four major classes based on the method by which heat is applied to produce oil, as follows:

Class	Method of Heat Application	Examples
I	Heat is transferred to the shale through a wall	Pumpherstons; Hayes; Berg
II	Heat is transferred to the shale from the combustion occurring in the retort by burning product gases and the residual carbon in the retorted shale	N-T-U; Union Oil Co.; Pintsch; Bureau of Mines Gas-Combustion
III	Heat is transferred to the shale by passing previously heated gases or liquids through the shale bed	Swedish Industrial; Bureau of Mines Gas-Flow; Royster
IV	Heat is transferred to the shale by introduction of hot solids into the retorting bed	Standard Oil Co. Fluid-Flow; Bureau of Mines Hot-Solids-Contact

A number of retorts of the various classes have been studied and tested at the Bureau of Mines oil-shale demonstration plant.

Class I Retorts. A Pumpherston retort was used in the pilot plant investigations at Rifle from 1925-29 and was operated experimentally to determine the suitability of this retort for processing Green River oil shale. Pumpherstons have been used to produce shale oil and ammonia in Scotland for over 50 years and have also been used in France and Australia.

The retort consists basically of a cylindrical inner vessel of firebrick which is surrounded by an outer firebrick shell. The space between the two structures is divided into several combustion chambers. The inner vessel is charged with oil shale, and retorting heat is supplied from burning the fixed shale gas, which is recovered during the retorting operation in the combustion chambers. The heat is transferred through the inner fire wall to the shale. Raw shale is fed into the top of the retort intermittently and discharged continuously from the bottom. Steam is admitted to the bottom of the retort, flows up through the shale bed, and leaves the retort with the shale oil vapors and gases, which are drawn by turboexhausters through the condensing and scrubbing system.

Noncoking American shale progressed satisfactorily in the Pumpherston and recovery of oil averaged 89.3% of the assay value. However, the retort became plugged when richer shales were retorted, and the Pumpherston was found generally unsatisfactory for processing Green River oil shale. Additional dis-

advantages include a comparatively low production rate in relation to capital expenditure and required operating labor and relatively inefficient heat transfer. In Scotland, the production of good yields of ammonia, in addition to oil, offsets the disadvantage of inefficient heat transfer.

During 1946, the Bureau of Mines conducted experimental operation with a low temperature coal-carbonization pilot plant known as the Hayes retort. This work was done in cooperation with the Colorado Fuel & Iron Corp. at the company's plant in Pueblo, Colo. The tests were primarily made to produce crude shale oil for laboratory investigations prior to the completion of the retorting plant at Rifle. The Hayes retort consists essentially of a rotating tube containing a screw conveyor. The retort tube is set in a furnace and the oil shale is carried through the tube by the screw conveyor. Oil vapors are drawn from the retort into a condensing system by an exhaustor operating at a slight suction. Although no difficulties were encountered due to coking, yields were poor and the shale oil contained large quantities of dust formed by the breakage of shale as it traveled along the screw conveyor. Heat transfer through the metal shell was also slow, and high capital and operating costs precluded consideration of the Hayes as a commercial retort.

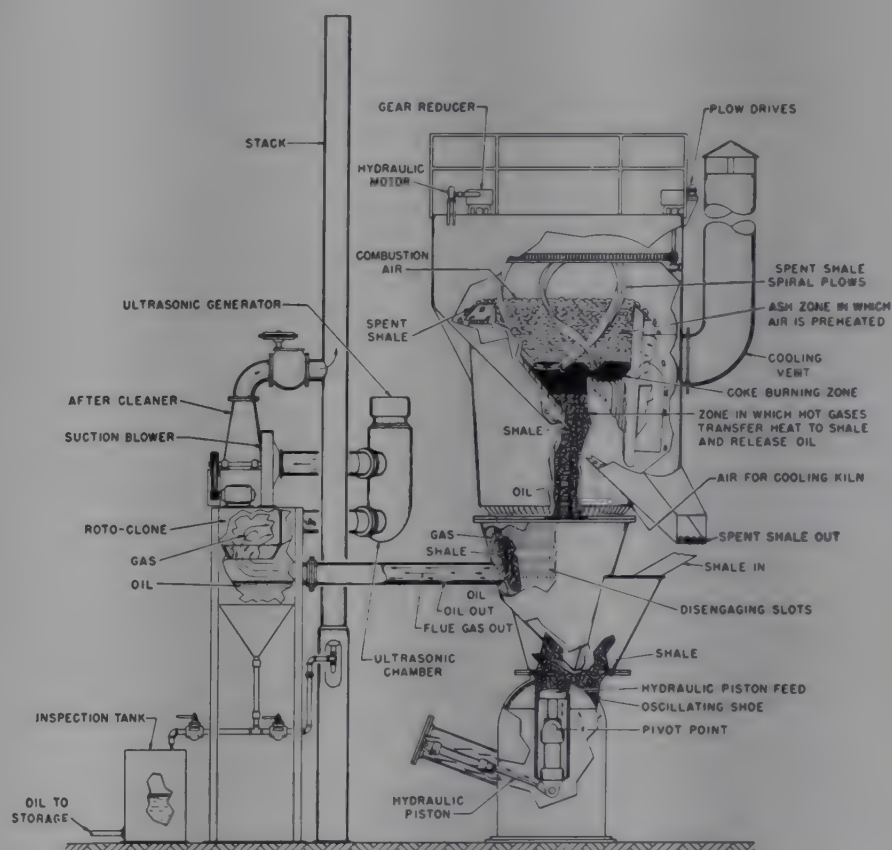


Figure 5. Retort Developed by Union Oil Co. of California

Class II Retorts. The Nevada-Texas-Utah retort, commonly called the N-T-U but also known as the Dundas-Howe retort, was invented and developed in the United States (5) and has been used in commercial operations in Australia and England. Two N-T-U's were constructed at the Oil-Shale Demonstration Plant for the purpose of studying retorting rates, heat transfer, and other thermodynamic relationships with plant size equipment and to develop retorting techniques, train personnel, and produce shale oil for other experimental operations. It is to be emphasized that the batch N-T-U is not considered or suggested as a practical retort for a commercial operation in the United States, but it has been used as a tool for gathering fundamental data. Nevertheless, it has played an important role in providing a fund of plant operating experience that is applicable to other processes, and its use has contributed greatly to a better knowledge of shale handling, maintenance of equipment, and design of equipment to meet the peculiar needs of Colorado oil shale and shale oil.

The N-T-U retorting and condensing system consists of the retort, a shale trap, a contact condensing system, a reflux accumu-

lator, air and gas blowers, and a waste gas stack (Figure 3). The retort is a cylindrical steel vessel with tapered firebrick lining and dome (Figure 4). The inside diameter of the retort is 10 feet 4 inches, tapering to 8 feet 8 inches at the top, with a dome radius of 4 feet 4 inches and an over-all height of 22 feet. A manhole is provided at the top for charging, and the bottom is closed by a hinged grate operated through a toggle mechanism and carriage

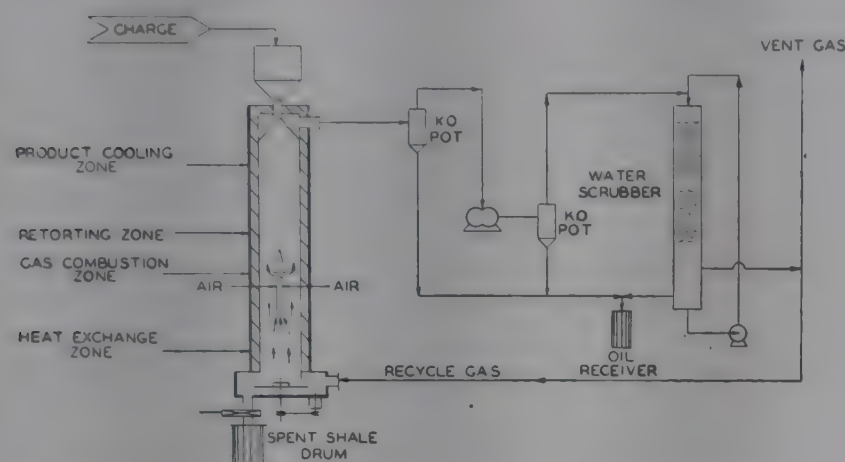


Figure 6. Flow Diagram of Gas Combustion Retorting Plant

by a hydraulic cylinder. Each of the two retorts holds approximately 40 tons of shale. A gas seal between the grate and retort is provided by filling a channel-shaped ring on the grate periphery with clay-oil luting.

The N-T-U batch-type retort is operated on a cycle which consists of charging, running, and discharging. After the retort is charged with approximately 40 tons of shale (-3.5 to $+0.5$ inch), a fire is started on the top of the shale bed using approximately 200 pounds of oil-soaked kindling. The manhole is left open and a draft is drawn downward through the shale bed by the gas blower. As soon as combustion is under way, the manhole is closed, and air is forced into the top of the retort with the air blower. The air stream is diluted with combustion gas in the retort. Excess gas is vented to the atmosphere through the waste gas stack. Retorting takes place below the combustion zone because of the hot gases passing downward through the shale bed. In the retorting zone, shale-oil vapor, fixed gases, and coke are formed by destructive distillation of the kerogen, and the coke remaining in the shale serves as fuel when the downward moving combustion zone reaches it. Some of the oil vapor condenses on the cold shale in the lower part of the retort and is removed from the system through the shale trap. The condensed oil removed at this point amounts to about half of the oil produced, the balance being recovered in the condensing system. After the charge has been retorted, the blowers are shut off and the spent shale is discharged by opening the hinged bottom.

Following experimental tests, the N-T-U retorts were operated on a production basis to determine the significance of operating variables and their relationship to the entire operation. At a retorting rate of 35 pounds of shale per hour per square foot of retort cross section, a maximum recovery efficiency of 90% of Fischer assay was obtained. The best oil recovery rate was 110 gallons per hour, which was obtained with no recycle gas and an air rate of 1000 superficial cubic feet per minute corresponding to the optimum gas velocity of 15 superficial cubic feet per minute per square foot of cross-sectional area. The superficial gas velocity is calculated at standard conditions assuming the retort empty.

In retorting systems such as the N-T-U and Union Oil Co. processes, definite benefits are realized through the "down burning" of the oil shale. These advantages include: (1) gravity flow of the oil produced to the product withdrawal point at the bottom of the retort; (2) better heat economy by concurrent condensation of the oil vapors on the cold shale in the area below the combustion zone and preheating of the shale in this area; and (3) better heat transfer to those shale particles which are wet with shale oil.

Union Oil Co. Retort. A continuous, internally fired, under-feed retort has been developed by the Union Oil Co. of California, and a 50-ton semiworks unit has recently been formally

demonstrated at the company's Wilmington, Calif., refinery. The demonstration was carried out under simulated commercial plant conditions, and representatives from the Bureau of Mines and other governmental agencies as well as observers from numerous oil and construction companies in the United States, Brazil, and England were in attendance. The shale processed in the retort was from the Green River formation in Colorado and was obtained through the cooperation of the Bureau of Mines.

Process flow and pertinent structural features of the semiworks Union retort are illustrated diagrammatically in Figure 5. Raw shale is fed upward through the bottom of the retorting vessel by a hydraulically operated piston which oscillates through an arc between the shale charge hopper and the retort. The entire feeding mechanism is submerged in oil to the level of the transfer line, providing both a liquid seal to prevent air from entering through the feed hopper and lubrication of the moving parts. Shale moves countercurrent to a stream of air which enters through the top of the vessel. Residual carbon in the shale is burned in the upper portion of the retort, and the hot combustion gases flowing down through the shale bed heat the incoming shale. As the shale moves upward through the retort, it passes through a cool zone where oil condenses, then to a retorting zone where the temperature is raised to 900°F. , to a combustion zone where residual carbon is burned from the oil-free material and the temperature raised to 2000°F. , and finally through a zone at the top of the retort where the spent shale is cooled to 800°F. by the incoming air, and the air is thereby preheated. Liquid distillation products are withdrawn from the bottom of the unit, and ash and clinker are removed overhead by a revolving plow mechanism.

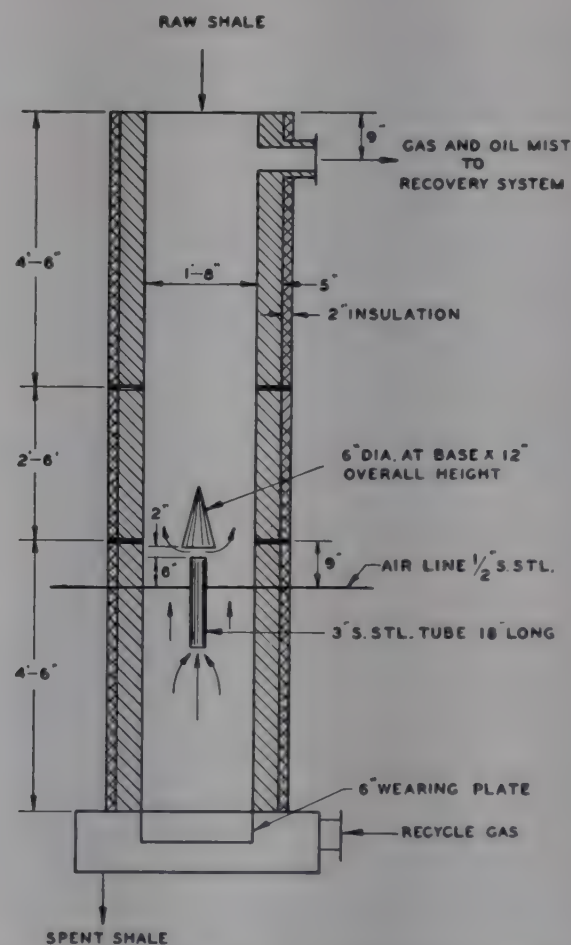


Figure 7. Gas Combustion Oil-Shale Retort

The Union Oil Co. retort represents a distinct departure from conventional retorting processes and has the advantage of requiring no condensing equipment and no combustion or heat transfer facilities outside the retort. In addition, it has been demonstrated that the full range of particle size and fines produced in crushing of shale can be efficiently processed in the unit. The ability of the Union retort to tolerate fines, which normally cause plugging and excessive clinker formation, is attributable to the continuous nature of the moving bed and the action of the plows which control particle size in the area of clinker formation, termed the plastic ash zone. These advantages contribute materially to a low capital investment in a commercial retorting plant as well as to decreased mining costs and handling problems.

TABLE III. GAS COMBUSTION RETORTING DATA SUMMARY

(Heat and material balances)

Run No.	60		61		62		63		64		65		66		67	
Material balances (lb./ton raw shale)	Lb./ton	%	Lb./ton	%	Lb./ton	%	Lb./ton	%	Lb./ton	%	Lb./ton	%	Lb./ton	%	Lb./ton	%
In																
Raw shale	2000	91.7	2000	88.8	2000	85.2	2000	82.4	2000	84.2	2000	86.2	2000	85.8	2000	90.2
Air	182	8.3	254	11.2	350	14.8	427	17.6	376	15.8	320	13.8	329	14.2	220	9.8
Total	2182	100.0	2254	100.0	2350	100.0	2427	100.0	2376	100.0	2320	100.0	2329	100.0	2220	100.0
Out																
Spent shale ash	1740	79.8	1650	73.3	1542	65.7	1554	64.0	1548	65.2	1614	69.6	1672	71.8	1738	78.3
Product gases	218	10.0	354	15.7	532	22.6	618	25.5	597	25.1	558	24.1	500	21.5	332	15.0
Oil	76	3.5	164	7.3	152	6.5	146	6.0	151	6.4	154	6.6	158	6.8	165	7.4
Condensed water	4	0.2	15	0.7	10	0.2	11	0.5	11	0.5	9	0.4	5	0.2	4	0.2
Unaccounted for	144	6.5	71	3.0	114	...	98	4.0	69	2.8	-15	-0.7	-6	-0.3	-19	-0.9
Total	2182	100.0	2254	100.0	2350	100.0	2427	100.0	2376	100.0	2320	100.0	2329	100.0	2220	100.0
Heat Balances (B.t.u./ton raw shale)	B.t.u./ton	%	B.t.u./ton	%	B.t.u./ton	%	B.t.u./ton	%	B.t.u./ton	%	B.t.u./ton	%	B.t.u./ton	%	B.t.u./ton	%
In																
Heat of combustion	254000	91.2	355000	94.2	487500	95.7	595000	97.1	543000	96.5	456000	95.8	458000	95.8	309000	92.5
Sensible heat of air	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sensible heat of recycle	24400	8.8	21900	5.8	22150	4.3	17880	2.9	20000	3.5	20000	4.2	20300	4.2	25000	7.5
Total	278400	100.0	376900	100.0	509650	100.0	612880	100.0	563000	100.0	476000	100.0	478300	100.0	334000	100.0
Out																
Sensible heat of ash	30450	10.9	54580	14.5	40100	7.9	78200	12.8	69600	12.4	41900	8.8	53500	11.2	34760	10.4
Sensible heat of gas	40500	14.6	34700	9.2	39100	7.7	37400	6.1	38400	6.8	36600	7.7	33500	7.0	44000	13.2
Sensible heat of liquid	2591	0.9	6005	1.6	5240	1.0	6626	1.1	5000	0.9	5000	1.1	5000	1.0	5600	1.7
Heat of vaporization of H ₂ O	37800	13.6	28000	7.4	30600	6.0	28400	4.6	29900	5.2	32700	6.9	40500	8.5	36800	11.0
Heat of reaction of kero-gen	25100	9.0	41800	11.1	40400	7.9	39400	6.4	41200	7.3	40400	8.5	41400	8.7	42200	12.6
Carbonate decomposition	87600	31.5	120000	31.8	180700	35.5	264800	43.2	234000	41.6	196000	41.2	129000	27.0	105700	31.6
Heat loss by diff.	54359	19.5	91815	24.4	173510	34.0	158054	25.8	144900	25.8	123400	25.8	175400	36.6	64940	19.5
Total	278400	100.0	376900	100.0	509650	100.0	612880	100.0	563000	100.0	476000	100.0	478300	100.0	334000	100.0

through utilization of the fines. A description of the 50-ton semi-works unit has been published (12).

Gas Combustion Retorting Process. The Bureau of Mines is currently investigating a vertical countercurrent retorting process in a 500-pound-per-hour pilot plant. This process has several novel features that depart from former concepts of retorting. Although simple mechanically, it is capable of a high yield of liquid products at high shale throughput rates. It is indicated that cost figures for the process will be less than for other retorting processes studied to date.

A schematic flow diagram of the pilot plant process is shown in Figure 6. A portion of the product gases is introduced at the bottom of the retorting vessel. These gases pass up through the bed of descending hot spent shale and recover the sensible heat from this material. A portion of the preheated gases then passes up through the stainless steel tube and is mixed with air introduced through opposite sides of the tube. This mixture of air and gases passes out under the cone into the shale bed where combustion of the combustible constituents in the gas and a small amount of the carbonaceous residue remaining on the spent shale takes place. Enough air is introduced to provide the minimum of heat required by the process. The resultant hot flue gases from the combustion section pass up through the shale bed and cause the shale to be heated to retorting temperature. The oil is released from the shale presumably as a vapor and is swept away by the flue gas stream to the heat exchange zone where the gas stream is cooled; most of the oil vapors are condensed as a very fine stable mist and are carried out of the retort by the gas stream in this form. A small portion of the oil vapors condenses on the surface of the shale particles. This material is revaporized in the retorting zone.

The liquid products are recovered from the gas stream by passing the mixture through a centrifugal separator, a positive displacement blower, a second centrifugal separator, and a concurrent water scrubber. Ordinarily 25 to 35% of the liquid products are recovered in the first separator, 60 to 70% in the second separator, and 2 to 10% in the concurrent water scrubber. Since some gas is produced in the process, part of the gas stream must be vented, and the balance is recycled.

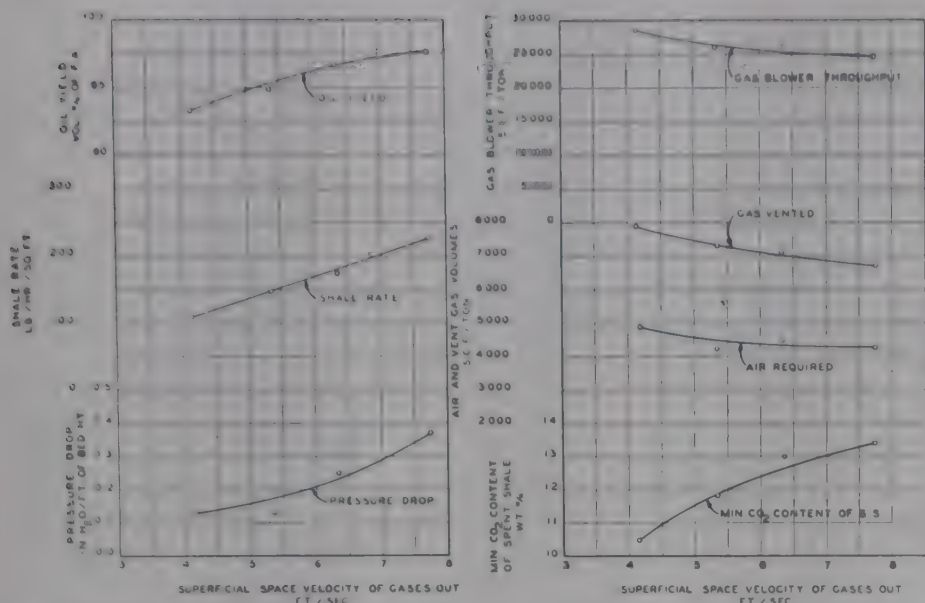
The essential features of the retorting vessel are shown in Figure 7. The vessel proper consists of three flanged steel sections 30 inches in diameter lined on the inside with 5 inches of insulating refractory and 2.5 inches of insulation on the outside. The total height of the three sections is 12 feet. However, a 6-inch steel wearing plate is attached to the lower flange and an 8-inch diameter feed leg extends down 18 inches from the top so that the depth of the shale bed is actually about 11 feet.

Raw shale is charged through twin hoppers mounted on the top of the retorting vessel. Each of the hoppers has a capacity of about 350 pounds of raw shale. The raw shale is conveyed from floor level in buckets to the hopper platform by use of an electric hoist mounted on the roof beams. The hoppers discharge the raw shale into the vessel through an 8-inch feed pipe.

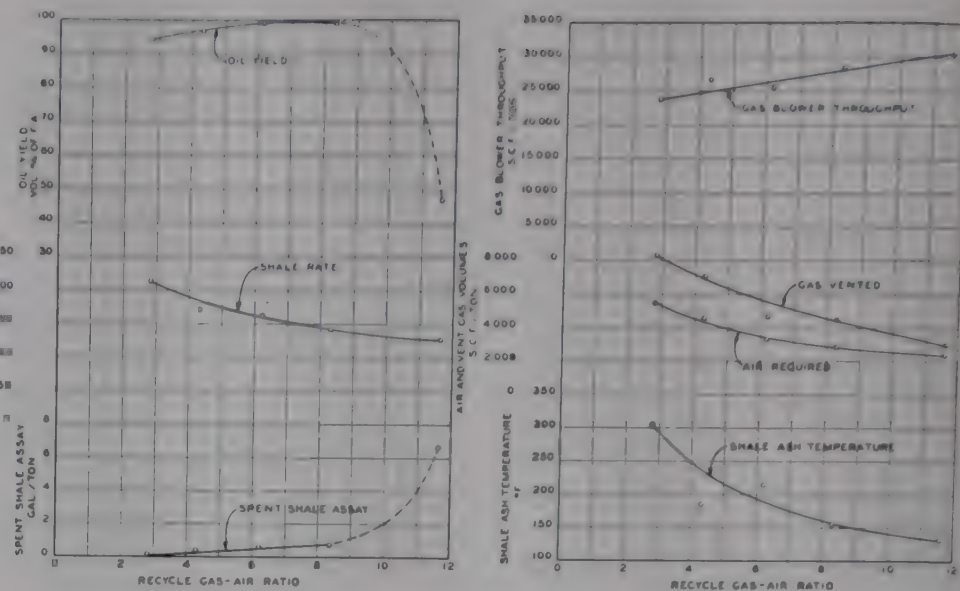
Shale ash is discharged from the retorting vessel by means of a rotating disk driven by a variable speed direct current motor. The disk is enclosed in a pressure-tight housing into which the recycle gases are injected. The ash is carried to a common discharge point in the housing by chains attached to the outer edge of the disk. The ash drops through a slide valve into removable 55-gallon drums flanged to the slide valve for easy removal.

Two centrifugal separators are used in the recovery system for separating the product oil from the gas stream. A packed concurrent water scrubber is located in the recovery system after the second centrifugal separator. The capacity of the two blowers, which are operated in parallel, limits the maximum shale rate at which the retort can be operated at the present time.

Another distinct advantage of the process is that elaborate instrumentation is not required. Two temperature strip-chart recorders are used for the necessary temperature measurements and all process flows and pressures are measured by U-type manometers. Gas flows and pressures are controlled by manual positioning of butterfly valves.



Figures 8 and 9. Operating and Yield Data for Constant Shale Grade and Recycle Gas-Air Ratio



Figures 10 and 11. Operating and Yield Data for Constant Shale Grade and Inlet Gas Velocity

During normal operation of the pilot plant unit, the air and recycle gas rates are maintained constant. Since the air rate is constant, the amount of heat released from combustion is also approximately constant. The temperature of the product stream leaving the retort can thus be controlled indirectly by changing the temperature of the ash discharged. This is accomplished by varying the rate at which ash is discharged from the retort. The net effect is to move the temperature profile of the retort up or down. Shale from the upper bench of the experimental mine was used for the gas combustion runs reported here since it was available at the time. However, middle-bench shale has been successfully processed in the countercurrent retort and no operational difficulties were encountered.

Operating and yield data for a series of pilot plant runs have been correlated and are presented in Figures 8 through 11.

Figure 8 shows that for a constant recycle gas-air ratio and constant shale grade increasing the space velocity of the gases out of the retort causes a gradual increase in the efficiency of the liquid oil recovery from the shale. The shale rate increases linearly and the pressure drop through the bed increases at a greater rate. From these data it is believed that a satisfactory oil recovery could be realized at much higher shale rates than those studied to date.

The effect of space velocity on the gas volumes and mineral

carbonate decomposition is shown in Figure 9. The curves indicate that at the higher space velocities less heat input is required; this is reflected in the lower air requirements and gas volumes. Likewise, at the higher space velocities the shale is subjected to the combustion zone temperature for a shorter period of time and less mineral carbonates are decomposed.

In Figure 10 the effect of recycle gas-to-air ratio on the oil yield, spent-shale assay, and the shale rate is shown. The oil yield improves at a gradual rate with increasing recycle gas-to-air ratio until a point is reached at which the bed temperatures drop to such a level that complete retorting is not realized. Although the inlet gas space velocity was constant for these runs the outlet gas velocity was not, and this also has influenced the shape of the shale rate relationship. However, it is apparent that the ratio can be varied over a wide range without influencing the oil yields appreciably. The relationship of other process variables are shown in Figure 11.

Material and heat balances for each of the runs are presented in Table III.

Class III Retorts. A Royster retort was the first in this class to be operated at the oil-shale demonstration plant. This is a batch process in which the uncondensed gas from the distillation



Aerial View of N-T-U Retorts

Crushing plant at right; three raw shale storage bins are between crushing plant and retorts

TABLE IV. GAS-FLOW RETORTING SUMMARY

(Effect of recycle-gas inlet temperature on retorting conditions and yields)

	Low Tempera- ture	High Tempera- ture
Shale processed		
Fisher assay, gal./ton	21.5	21.5
Mineral CO ₂ content, wt. %	16.9	16.9
Particle size, inches	0.5-1.0	0.5-1.0
Retorting conditions		
Shale charge rate, tons/day	12.4	18.6
Shale residence time, min.	60	40
Recycle-gas velocity ^a , ft./sec.	0.5	0.5
Recycle-gas, thous. stand. cu. ft./ton shale	50.8	34.4
Recycle-gas inlet temperature, ° F.	1075	1350
Temperature retorted shale, ° F.	955	1020
Heat transferred to shale, B.t.u./lb. shale	283	317
Heat-transfer rate, B.t.u./lb. shale/min. residence time	4.8	7.9
Product yields		
Oil ^b (Fischer assay), vol. %	107	100
Oil, gal./ton	22.9	21.5
Gas, cu. ft./ton shale	833	1277
Product gas components		
Hydrogen	288	404
Hydrocarbons ^c (principally methane)	241	171
Unsaturates	38	33
Carbon monoxide	113	352
Hydrogen sulfide	3	1
Carbon dioxide	80	193
Water vapor	70	123

^a Velocity of gas corrected to standard conditions passing through empty retort.^b Water- and sediment-free basis.^c From Orsat analysis; other alkanes are possibly present, but mass spectrometer analyses on similar gases show methane to predominate.

of shale is circulated through a heater, the retort, and the oil recovery system. A pilot plant was operated in 1948 and the results have been reported in considerable detail (17). The Royster process is not considered to have commercial possibilities, principally because it is a batch operation. However, it led to the development of a similar process which is continuous in operation and has definite commercial possibilities; it is known as the gas-flow retorting system.

The gas-flow process is shown in Figure 12. Crushed raw shale, 0.25 to 1 inch in particle size, enters the top of the retort through a rotary gas seal. The shale flows by gravity through the retorting vessel, which is 10 feet high and 18 × 12 inches in cross section; it has a capacity of 1500 pounds per hour (Figure 13). Product gases, raised to a temperature of 1075° to 1350° F. in the propane-fired gas heater, enter the retort through a gas-distribution manifold and flow transversely through the moving bed of shale particles which is bound on two opposite sides by louvers. Conversion of the kerogen occurs as a result of the exchange of heat between the circulating gas stream and the shale. The inlet gas manifold distributes the gas to various portions of the shale bed in order to control the temperature gradient from the top to the bottom of the retort. Spent shale at 955° F. is discharged from the bottom of the retort by a vibratory feeder which also controls the shale throughput rate.

The circulating gas stream containing the oil, gas, and water produced during retorting passes through a scrubber where part of the oil is condensed and entrained shale is removed; product oil is used as the scrubbing medium. The overhead stream from the scrubber passes to a tubular condenser where the remaining oil and water are condensed. After repressuring, the excess make gas is vented through a pressure controller and burned; the heat-carrying gas required for retorting is recycled through the gas heater and back to the retort. A part of the cool recycle gas is by-passed around the gas heater and mixed with the hot gas stream from the heater to control the temperature of the gas entering the retort.

Experimental operations of the gas-flow pilot plant began in 1948 and are still in progress. The test program has included raw shale preheating studies, determination of the optimum outlet shale temperature, and the study of the effect of recycle gas inlet temperature. The shale preheater, originally mounted above the retorting vessel, was removed after tests indicated poor heat economy and other disadvantages. For residence periods of 55 minutes and longer, the oil content of the retorted shale is low when the shale is heated to temperatures above 925° F.; for resi-

dence periods of less than 55 minutes, the oil content of retorted shale having an outlet temperature of 925° F. is greater. Tables IV and V show the effect of recycle gas inlet temperature on product yield and quality, and on circulating gas requirements and energy consumption.

The crude shale oils from the low and high temperature runs were very similar, as shown in Table V. Gas-flow oil appears to be similar to N-T-U and Royster shale oils, except that it is somewhat heavier.

In a commercial plant, the gas produced by the gas-flow process could be utilized to generate power, burned in gas engines or turbines, or under steam boilers. Should it be desirable to generate power and heat from other sources, the shale gases could be used as a source of hydrogen for a hydrogenation step in refining or as a source of synthesis gas for the production of liquid fuels by Fischer-Tropsch synthesis. In addition, the Fischer-Tropsch process would yield organic chemical by-products such as ethanol, propanol, butanol, acetic acid, propionic acid, acetone, methyl ethyl ketone, and acetaldehyde.

Preliminary operation has been conducted with a spent-shale burner, using cool retorted shale from the gas-flow pilot plant. The tests indicate that retorted shale will support combustion, and that by using recycle gas, the combustion temperature can be controlled to minimize carbonate decomposition. Approximately 61 B.t.u. are generated per pound of retorted shale, and using a spent-shale burner receiving hot retorted shale directly from the retort, this quantity of heat plus the sensible heat in the hot shale charged to the burner would be sufficient to retort an equivalent amount of raw shale.

Class IV Retorts. The Standard Oil Development Co. has developed a fluidized method of retorting (Figure 14). Tests have been conducted on a pilot plant, previously used for experimental work on fluid catalytic cracking of petroleum fractions, which has been converted to an oil-shale retorting pilot plant. Under a cooperative agreement, the Bureau of Mines has furnished the company 1000 tons of -3/16-inch shale for this work.

TABLE V. GAS-FLOW RETORTING SUMMARY

(Effect of recycle-gas inlet temperature on products)

	Low Tempera- ture	High Tempera- ture
Product gas ^a		
Molecular weight	16.2	19.7
Net heating value, B.t.u./cu. ft.	474	340
Composition, mole %		
Hydrogen	34.6	31.6
Methane	28.9	13.2
Ethane	0.0	0.2
Unsaturates	4.6	2.6
Carbon monoxide	13.6	27.6
Hydrogen sulfide	0.3	0.1
Carbon dioxide	9.6	15.1
Water vapor	8.4	9.6
Retorted shale		
Organic residue content, wt. %	1.4	1.9
Crude oil		
Gravity, ° A.P.I.	17.1	17.3
Viscosity, S.U.S. at 130° F.	234	245
Viscosity, S.U.S. at 210° F.	57	58
Pour point, ° F.	85	80
Flash point (C.O.C.), ° F.	260	260
Conradson carbon, wt. %	5.5	6.0
Sulfur, wt. %	0.7	0.7
Nitrogen, wt. %	2.2	2.2
Water, vol. %	9.8	12.0
Sediment, wt. %	1.9	3.0
100 ml. distillation (cor. to 760 mm.), ° F.		
Initial boiling point	225	235
% recovered		
2	426	436
5	463	466
10	507	508
20	582	584
30	616	615
40	630	629
50	641	638
60	651	653
70	660	662
Overhead recovery, %	77	75

^a Corrected for air and flue-gas leakage.

In this process, raw shale is charged continuously to a fluidized bed in the retort. Gas, oil, and water are removed overhead through a cyclone and recovered. The retorted shale, stripped of residual liquid hydrocarbons, is discharged from the retort and carried by a stream of air to the fluidized combustion chamber, where the retorted shale is burned. A stream of hot ash from the burner is mixed with steam and fed to the retort to provide heat for retorting. Another stream of ash is withdrawn continuously from the burner and disposed of as waste. The unit may also be operated as a single-vessel system in which burning and retorting take place in the same vessel.

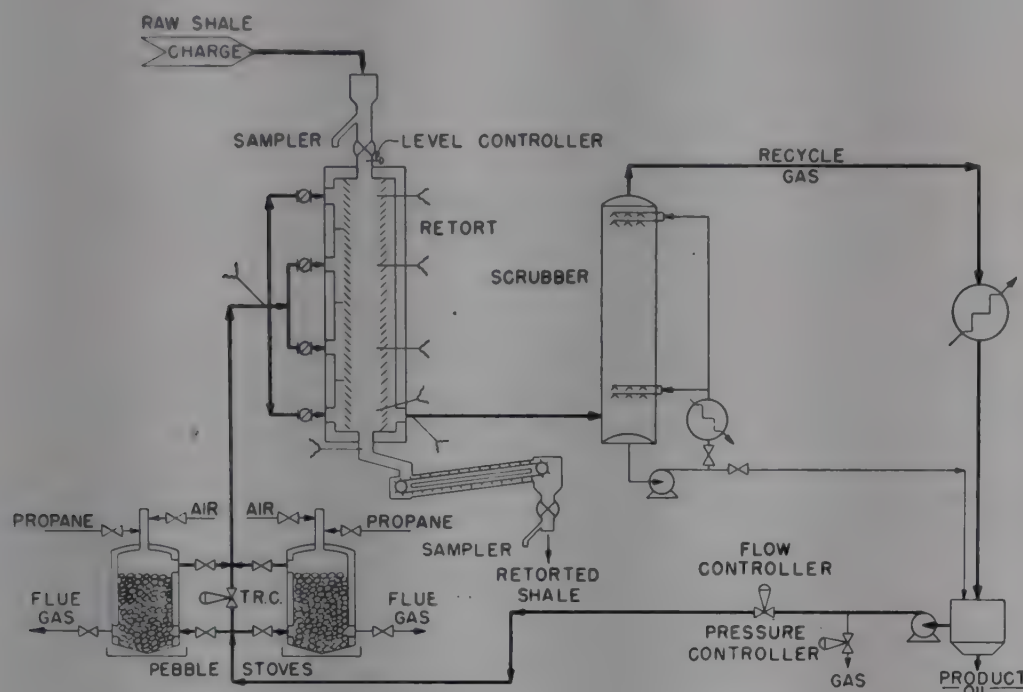


Figure 12. Flow Diagram of Bureau of Mines Gas-Flow Retorting Process

The fluid-flow process has the advantages of high-heat transfer rates which result in high throughput rates. Heat efficiency should be high, since a fairly good fuel gas is recovered in addition to the oil. No moving parts are required for transporting the shale through the system, and maintenance costs should be reasonable.

Retorting Process in Design Stage. The pilot plant design of a recently devised continuous retorting process is under way at the demonstration plant at the present time. The hot-solids-contact process combines the principle of solid-to-solid heat transfer with the use of cold shale as a cooling medium for oil vapors produced during retorting, and uses the residual carbon on retorted shale to supply the heat for retorting. It is anticipated that the process will retort shale fines as well as coarse particles, since the velocity of the gases will be low enough that there should be no tendency for the gas stream to carry fines from the retort. Power requirements are also estimated to be smaller than for processes using hot gases as the medium for carrying heat to the shale.

NATURE AND CHARACTERISTICS OF SHALE OIL

The characteristics of crude shale oil as produced in retorts vary to a considerable extent depending on the nature of the organic material in the shale and the retorting process used. In general, the crude oil is a black, waxy oil having a gravity of about 21° A.P.I. and, because of its high wax content, a pour point of about 90° F. It is composed chiefly of hydrocarbons, consisting of olefins, paraffins, naphthenes, and aromatics; appreciable amounts of sulfur, nitrogen, and oxygen compounds are present but no light ends.

Table VI compares the properties of Colorado shale oils produced by several retorting processes. The oils from all processes in which the shale is heated by passage of hot gas through the shale bed are quite similar but differ from those produced by a process in which heat is transferred through a metal wall. In some of its physical and chemical properties, the oil resembles coal

tar, and in some it is quite similar to petroleum. In other respects, it is different from both coal tar and petroleum.

Coal tar has a specific gravity of 1.192 and sulfur content of 0.04 or less. Volume percentages of acid oil, middle oil, heavy oil, and pitch in typical coal tars average 16, 25, 12, and 47%, respectively. However, this is not a good comparison since the light oil, representing 1% of the products from the coking of coal, is absent from coal tar. Properties of a typical mid-continent crude are included in Table VI. Important differences between shale oil and petroleum are the shale oil's higher percentages of olefins, aromatics, and compounds of sulfur, nitrogen, and oxygen and lower percentages of paraffins and naphthenes. As compared to petroleum, shale oil is also deficient in hydrogen, owing to its unsaturation.

REFINING

Using conventional equipment, shale oil will yield a range of acceptable fuel oils by relatively simple refining. Crude shale oil from the N-T-U retorts has been used to fire the boilers at the oil-shale demonstration plant and has proved to be very satisfactory. However, the manufacture of motor and Diesel fuels with yields and qualities comparable to petroleum is not as simple and requires a different approach from that of petroleum refining.

The refinery at the oil-shale demonstration plant is designed so that atmospheric distillation, reforming, single-coil recycle cracking, visbreaking, or delayed coking can be performed with minimum changes in the refining equipment.

The refinery was designed as the smallest semi-commercial plant that could be constructed using conventional petroleum refining equipment. It has a capacity of 300 barrels per stream day based on the minimum practical size of heater tube that could be utilized under the conditions of the various proposed operations.

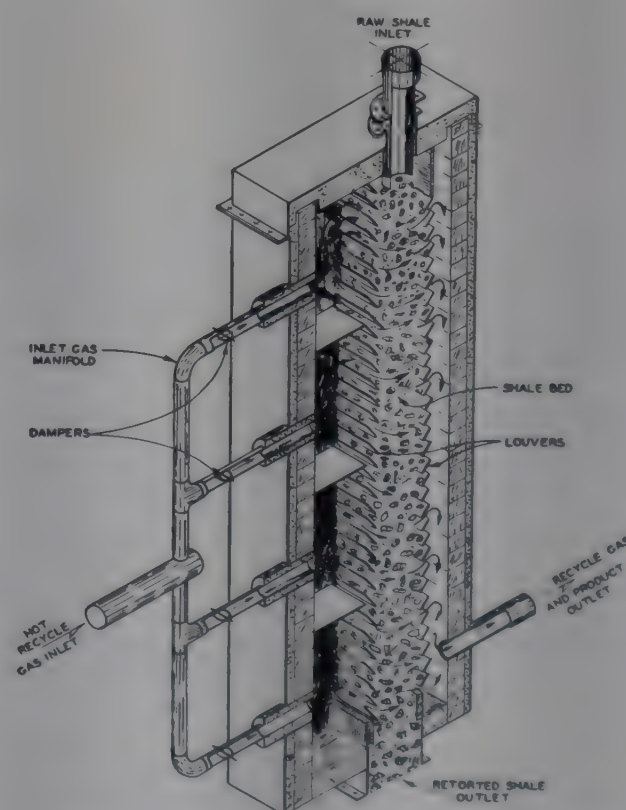


Figure 13. Gas-Flow Retorting Vessel

The refinery consists of the following equipment:

1. A single-coil cracking furnace designed to operate under all conditions of atmospheric distillation, thermal cracking, and reforming. The cell-type upshot heater incorporates features for maximum flexibility, heat distribution control, and maintenance

TABLE VI. PROPERTIES OF COLORADO SHALE OILS

Retort	Sp. gr., 60°/60° F.	S, Wt. %	N, Wt. %	Pour Point, ° F.	Hempel Distn. Yields, Vol. %			
					Naph- tha	Light dist.	Heavy dist.	Resi- due
Gas-flow	0.9561	0.73	2.12	85	2.5	15.5	26.4	54.1
Royster	0.9267	0.72	1.95	95	5.0	16.0	35.6	42.1
Hayes	0.9248	0.80	2.50	55	26.2	20.3	30.2	20.6
Parry	0.9321	0.87	1.81	65	14.9	20.4	37.1	27.2
N-T-U	0.9321	0.79	2.10	90	2.6	16.5	31.2	48.3
Pumpherson	0.8930	0.77	1.57	60	17.6	29.4	40.0	12.7
Typical mid-continent crude	0.8293	0.14	..	5	28.4	25.0	18.6	26.3

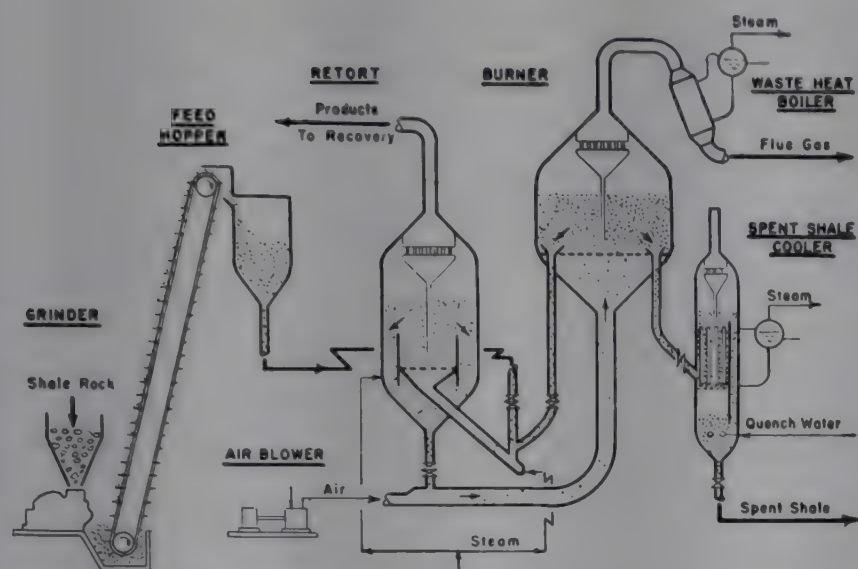


Figure 14. Fluid Shale-Oil Retorting Process Developed by Standard Oil Development Co.

simplicity. Flexibility is obtained by a system of external conversion piping which provides for three possible flow schemes through the heater.

2. Two coke chambers: One of these is suitable for 330 pounds per square inch pressure at design temperature and is used as either a cracking-reaction chamber during recycle-cracking operations or as a coke drum during coking. The second vessel has a design pressure of 125 pounds per square inch and is used for coking only. The capacity of the chambers was based on a 48-hour cycle, 24 hours being allowed for cooling and decoking. Winch and cable-coking equipment are used in the interest of economy.

3. A flash-fractionator which will separate the oil into gasoline, light gas oil, heavy gas oil, and heavy fuel oil. The flash-fractionator is 30 inches in diameter and 37 feet high, and is over a 42 × 29 foot flash chamber. The fractionating column contains sixteen bubble decks and two side-to-side pans.

4. A side-cut stripper for removing light components from the Diesel fraction. The stripper is a column 10 inches by 6.75 feet, packed with Raschig rings and mounted on a kettle-type reboiler. The light ends are stripped from the side-cut light gas oil fraction either by reboiling or by the use of steam.

5. An absorber to recover the liquefiable portions of the gases produced in cracking. The absorption column is 8 inches by 20 feet and is packed with 0.75-inch Raschig rings.

6. A stabilizer to remove excessive quantities of butane and any lighter hydrocarbons from the naphtha, yielding a gasoline fraction of the desired vapor pressure. The stabilizer is 16 inches by 24 feet and is packed with 0.75-inch Raschig rings. Stripping heat is supplied by a conventional kettle-type reboiler.

7. A continuous low temperature acid-treating unit to provide for treating of motor fuel fractions for nitrogen, sulfur, color, and gum control.

8. A rerun distillation unit for removing high-sulfur polymers from the gasoline after the acid treatment. The rerun unit consists of a packed fractionator, 16 inches by 14 feet, with a reboiler, feed preheater, and the usual fractionating auxiliaries, including the overhead condenser, receiver, and reflux pump. Heat is supplied to the reboiler by a hot-oil circuit from the flash fractionator.

9. A continuous doctor sweetening unit to convert objectionable odorous components of the gasoline or other distillate fractions to sweet compounds.

The refinery was completed in 1949 and limited operations have been conducted. An accompanying article describes the

refining processes that have been investigated and presents preliminary data representative of the refinery's first production (8). Performance tests conducted with shale Diesel fuel and cracked shale-oil gasoline have indicated that the early products from the refinery are quite satisfactory. Table VII compares shale Diesel fuel with

petroleum Diesel fuel. The shale fuel was prepared by batch-treating visbroken light-gas oil and was used for a period of 1 month in the Diesel equipment in the experimental mine; this included three 15-ton dump trucks operated for 170 hours each and a fourth operated for 184 hours. The performance of the fuel under regular load and operating conditions was very satisfactory and comparable to the performance of commercial fuel normally used. On being dismantled, the engine of the fourth truck showed no unusual carbon or other fouling deposits and only normal wear of the fuel injection system. Dynamometer tests on the fuel showed greater engine horsepower output over the entire range of engine speed tests, a range of 1400 to 2100 engine r.p.m., as compared with the engine output when petroleum fuel was used. This confirmed the observations of drivers, who claimed greater power when using the shale fuel.

Limited performance tests have also been conducted with cracked shale-oil gasoline, which had been treated to approximate the specifications of commercial gasoline of petroleum origin. The gasoline was made from a composite of recycle cracked naphthas produced during the first refinery operations. The finished product has a sulfur content of 0.41% (Table VIII), but its color and storage stability were satisfactory after the addition of 0.005 weight % of Universal Oil Products No. 5 inhibitor. Though only a limited quantity of gasoline was made for the first road tests, its performance was entirely satisfactory. It is believed that cold weather use will require the addition of casing-head gasoline for greater volatility to improve starting characteristics. Although the fuel contained high percentages of olefins and aromatics, there was little audible detonation in the engine.

MATERIALS OF CONSTRUCTION (9)

Since a study of the corrosive characteristics of shale oil was desired, minimum material allowances were made for corrosion in the thermal processing unit of the refinery. Materials were selected primarily on the basis of strength requirements. It is be-

TABLE VII. COMPARISON OF SHALE OIL AND PETROLEUM DIESEL FUELS

Physical Properties	Shale Oil	Petroleum
Gravity, ° A.P.I. at 60° F.	36.0	38.8
Flash (Pensky-Martens), ° F.	198	130
Pour, ° F.	0	0
Viscosity, S.U.S. at 100° F.	36.6	36.8
Color ^a	8	-1
Conradson carbon (10% bottoms)	0.67	0.021
Sulfur, wt. %	0.66	0.18
Nitrogen, wt. %	0.12	Nil
Tar acids, vol. %	Nil	Nil
Tar bases, vol. %	Nil	Nil
Aniline point, ° F.	132.8	172.4
Diesel index	46.8	66.9
Cetane No. (motor)	48	54.5
A.S.T.M. distillation, ° F.		
Initial boiling point	415	340
20%	463	435
50%	508	492
90%	581	567
End point	638	638
Recovery, vol. %	99.0	98.0
Residue, vol. %	1.0	2.0
Loss, vol. %	0.0	0.0

^a National Petroleum Assoc. standard.

TABLE VIII. SHALE GASOLINE USED FOR PERFORMANCE TESTS

	Raw Gasoline	Treated Gasoline	Typical Petroleum Gasoline
Gravity, ° A.P.I.	53.5	58.0	59.0
Reed vapor pressure	7.8	5.6	8.5
Sulfur, wt. %	0.64	0.41	0.1
Nitrogen, wt. %	1.27	0.013	Nil
Tar acids, vol. %	1.6	0	0
Tar base, vol. %	6.6	0	0
Gum, A.S.T.M.	521.7	8.3	5.0
Doctor test	Sour	Sweet	Sweet
Induction period, min.	3-5	480+ ^a	480+
Corrosion copper strip	Neg.	Neg.	Neg.
Octane No. ^b (motor method)	71.7	71.3	73.0
Octane No. ^b (research)	78.6	77.9	78.0
A.S.T.M. distillation, ° F.			
Initial boiling point	108	117	90
10%	141	161	130
20%	202	190	180
50%	293	274	250
90%	395		370
End point	442	403	390

^a Gasoline contains 0.005 weight % U.O.P. No. 5 inhibitor.^b With 3.0 cc. of tetraethyllead per gallon.

lied that corrosion will not be severe since the sulfur compounds are of a less reactive type than those found in petroleum, and the nitrogen compounds have a corrosion-inhibiting effect.

The cracking heater tubes are 2% chromium and 5% molybdenum alloy, A.S.T.M. A 200-46, Grade 4, with fittings containing 2.25% chromium and 1% molybdenum. Tubes and headers are rated for 1000 pounds per square inch at 1050° F. In the transfer line and heater crossover connections, steel containing 4 to 6% chromium and 0.5% molybdenum, A.S.T.M. A 158-44T, p-5a, was used to give the desired tensile strength with some corrosion resistance. Pumps, exchangers, and control valves were all specified in accordance with the usual practice for high sulfur crude oils. None of the vessels is lined, but the coke drums and flash chamber are designed to permit the addition of ganister, a highly siliceous lining, if necessary.

Carbon steel is used throughout the chemical-testing plant except in dilute acid and ammonia handling equipment. The dilute acid and water settlers are lead-lined and served by Hastelloy B jet mixers and stainless steel pipe, Nos. 20 and 304. Carbon steel piping and cast-iron fittings are used in the ammonia refrigeration system.

Carbon steel is used throughout the N-T-U retorting plant, except in the water-cooled reflux oil cooler in the condensing system, where tube bundles made of Admiralty metal have replaced the original carbon-steel tubes because of the corrosive nature of water from the Colorado River. A firebrick lining is used in the N-T-U retorts as the temperature of the fire bed is 1800° to 2200° F. All firebricks are made of high heat-duty fire clay.

In the hottest parts of the gas-flow pilot plant, heat-resistant materials are used. In the pebble stoves there are two outer linings of insulating brick whose total thickness is 7 inches and one inner lining of firebrick 3.5 inches thick. The retort vessel is stainless steel, A.I.S.I. Type 304, and the louvers are cast-iron alloy specified to stand 1400° F. In a commercial plant, the retorting vessel would be made of mild steel with a refractory lining. Stainless steel was used as an expedient and for ease in operation. Brick-lined piping is used from the stoves to a point where the quench gas enters, and from this point to the retort, stainless steel is used.

FUTURE PROSPECTS

The Bureau of Mines' work at the oil-shale demonstration plant is directed toward the development of satisfactory processes and techniques for the commercial production of liquid fuels from oil shale. These methods will be made available to any American industry that may wish to engage in such an oil-shale industry.

Most of the major oil companies in this country own shale deposits and have displayed a keen interest in the work being done by the Bureau of Mines; many of the companies are engaged in cooperative work on oil shale and its products. Instead of being a competitive source of liquid fuels, oil shale actually is a supplement to those produced from petroleum.

The cost of finding new reserves and producing natural petroleum is increasing each year. The progress already attained in the short time devoted to the production of liquid fuels from shale indicates that steady advances are yet to be made with corresponding decreases in the costs of such fuels. The rising cost of liquid fuels from petroleum and the decreasing cost of liquid fuels from shale will meet some day, and although this day is as unpredictable as it is inevitable, it is thought by many that it will not be many years hence.



Multiple-Drill Jumbo for Drilling Heading on Top Level

ACKNOWLEDGMENT

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MODERN SULFUR MINING



View Over Top of Processing Plant; Sulfur Vat in Background

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A LONG the gulf coast of Texas and Louisiana are numerous "salt domes," from which comes 95% of this country's domestic elemental sulfur. These salt domes consist of a solid vertical column of rock salt, generally circular or elliptical in plan, extending underground from some unknown depth toward the surface. Overlying and extending upward from the top of the salt column lies a mass of rock usually consisting of anhydrite, gypsum, and limestone in the order named, and above these lie the normal sedimentary beds of sands, gravels, and clays. There may also be found sulfur—usually present as crystal seams and wall deposits in porous portions of the limestone or sometimes as disseminated particles in a limestone matrix—in concentrations varying from mere traces to more than 50%.

In the latter half of the 19th century several tragic failures at Sulphur, La., demonstrated the impracticability of mining sulfur from these salt dome deposits by conventional shaft methods. Herman Frasch then invented a process through which he was eventually able to develop a commercially acceptable means of

recovering sulfur from the buried porous cap rock of a salt dome and delivering it above ground as a product of suitable purity and condition for use. This consisted essentially of melting the sulfur in place by diffusing hot water in the formation and raising the melted sulfur to the surface by air lift. The following physical properties of sulfur have a decided bearing on the Frasch process:

Fusion temperature, about 115° C.
Specific gravity, nearly 2.0
Specific heat, only about 0.2
Viscosity, expressed as an undulating curve

From 120° to 150° C. the viscosity of liquid sulfur is comparable to that of water, but above this range, to 201° C., it increases to values where the sulfur does not flow readily and is difficult to pump.

The history and development of the American sulfur industry have been covered in detail by Mason (21), Haynes (10), Hanson (9), and in more concise form by Marshall (20). Waeser (29) has given a very complete bibliography of developments over the past several years. The Texas Gulf Sulphur Company, Inc. (26), and

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Butterworth (4) have provided general descriptions, profusely illustrated, of Texas Gulf Sulphur operations, and Dennis (5) has covered the history and methods of mining of Gulf sulfur-salt domes. This article develops a comparison between the sulfur-producing practices at the plant first constructed by Frasch for the Union Sulphur Company and the highly engineered practices of today, using the plant of the Duval Sulphur and Potash Company at Orchard Dome, Tex., as an example of modern sulfur mining. This plant was chosen because it affords a clear and accurate picture of present-day methods, and Duval generally operates on deposits of relatively short-term minability; these require more serious attention to equipment design in order that the plant may be moved, with minimum dismantling, to new locations as individual deposits are mined out.

SULFUR WELLS

Once a suitable salt-dome sulfur deposit and a dependable source of fresh water are available, the mining process is accomplished in three fundamental steps:

1. Operation of a power plant which can heat large quantities of water and pump it to the site of the field operations.
2. Distribution of hot water, by means of wells, to melt the underground sulfur and elevation of the melted sulfur to the surface.
3. Cooling and solidifying the sulfur.

In preparation for Frasch process mining, a well is drilled through the sulfur-bearing limestone, and several concentric strings of pipe are set in the hole; these are arranged with perforated sections and with rings separating one pipe from another so that hot water may be pumped into the sulfur formation through an outer string and liquid sulfur may be pumped up or water pumped down through an inner string, as conditions warrant. Drilling rigs and derricks used by Frasch were typical of that boom period of shallow oil drilling in the Gulf Coast. Steam boilers at the rig, or sometimes steam piped from the nearest heating plant, furnished the power, and drilling was by rotary methods. The particular feature that differs in comparison with modern rigs was the massive wooden derrick, customarily built on location and left over the completed well until it was abandoned. Today the Texas Gulf Sulphur Company—as an example of a large operator faced with considerable subsidence problems—leaves its steel derricks in place for use as workover rigs. Duval, on the other hand, in line with the smaller scope and more mobile requirements of its operations, mounts all its derricks on skids, using triple derricks as drilling rigs and double-decked or “pony” derricks as workover rigs. Table I is a comparison of pipe strings and water lines used in the first successful application of the Frasch process by the Union Sulphur Company at Sulphur, La., with present-day operations (13).

Since the heart of the Frasch process lies in the operation of these wells it is desirable to picture the events taking place underground which result in the fusion and collection of sulfur and its removal to the surface. The porous sulfur-bearing limestone of the caprock is at the start filled with cold water usually heavy with

dissolved solids, particularly sodium chloride and therefore is much heavier than fresh hot water, sometimes by as much as 20%. When the hot water is injected into the formation near the bottom of the well it immediately starts to work its way up, and the sulfur, as soon as it is melted, works its way down, stopping only when it reaches an impervious obstacle or a zone cold enough to resolidify it. The zone heated by the incoming water, therefore, tends to take the shape of an inverted cone with its apex at the bottom of the well. Outside the limits of the cone the temperature remains below the fusion point of sulfur, and sulfur droplets trickling down vertically will freeze when they pass

from the hot cone to the colder formation outside the cone. In this way the outer limits of the cone tend to become lined with resolidified sulfur, forming a natural bowl for conducting the liquid sulfur back to the well bottom. When sufficient liquid sulfur has collected in this bowl it will rise in the inner string of tubing, if the tubing is open to the atmosphere, and seek a hydrostatic level, usually about halfway to the surface. Air is then introduced into the column of sulfur through a small line hung in this inner string, and the resulting entrained mixture flows up through the string to the surface. The Freeport Sulphur Company periodically, when mining conditions are not suitable for economic production, uses a technique (16) somewhat different from the conventional method.

The mine of the Duval Sulphur and Potash Company at Orchard Dome, Tex., about 40 miles west and slightly south of Houston (flowsheet, page 2192) is in the caprock of the Orchard salt dome which was discovered in 1924 by the Gulf Production Company (2). This dome was prospected for sulfur by the Texas Gulf Sulphur Company with disappointing results. Gulf Production later, in drilling an oil test, drilled into the flank cap, and cuttings from this indicated the presence of sulfur in the deep flank cap. Duval then took over the sulfur rights, offset its drilling from the previous leads, and prospected new flank areas, uncovering enough sulfur to warrant building a plant. Steaming started January 27, 1938. Haynes (10) points out that the vagaries of sulfur mining were shown to their fullest extent here—one of Texas Gulf's poorest test holes just missed the richest portions of the Orchard ore body; if the drilling had been within a 50-foot radius of the test-hole it would have hit sulfur in quantity.

POWER PLANTS AND WATER HEATING

From his study of the physical characteristics of sulfur, modified by his initial experiences with his process, Frasch found that his mine water should be injected at about 330° F., and Union

TRADE GLOSSARY

- Bright sulfur** = sulfur which has been filtered or otherwise had organic contaminants removed, as distinguished from “off-color” sulfur
- Cake dropping** = removal of the clay-sulfur cake from the filter screens into the bottom of the filter
- Concentric strings** = lengths of pipe of decreasing diameter set concentrically in a well
- Flank cap** = cap rock on the flank of a salt dome
- Gut line** = small steam line carried inside larger sulfur line to keep sulfur in fluid state
- Kicker well** = a steaming well which, although not producing sulfur itself, is used, because of its location, in aiding sulfur production from other steaming wells
- Mine heater** = insulated kettle in which hot treated water is further heated to the temperature necessary for injection into steaming wells as mine water
- Mudding** = filling with ordinary clay the voids existing in porous limestone or left by extraction of sulfur; carried out to maintain pressure, reduce loss of hot process water, and assist in controlling its direction of flow
- Steaming well (actually a misnomer)** = term used to denote a well taking hot water
- Two-stage filtration** = filtration in which a mixture of crude sulfur and clay is passed through filters, building up a filter cake on the screens; through this a batch of untreated sulfur is pumped or preliminary partial decolorization prior to treatment with clay
- Workover rig** = mobile derrick and equipment for “trouble-shooting” at a well



Figure 1. Water-Treating Plant

Sulphur Company wells each took about 250,000 gallons of hot water per day. The general practice at Union was to operate a complete small water-heating plant for each well, with the plants scattered around the circumference of a 2000-foot circle enclosing the dome. Each plant was housed in a wood-framed, sheet-iron covered building with dirt floors and wooden walkways.

Water was brought several miles from the Houston River by open canal and lifted by steam injectors into a small open tank behind the boiler house. Exhaust steam from the plant pumps discharged into this tank through submerged open-end perforated pipes and heated the water somewhat; part of the warmed water was fed into a battery of duplex reciprocating piston-type boiler feed pumps and the remainder into a battery of outside-packed plunger-type reciprocating heater feed pumps. The heater pumps were connected in pairs to the tops of riveted steel vertical cylindrical heaters, 18 feet high and 30 inches in diameter. Water flowed down through the heaters over cast-iron trays, condensing live steam which was piped directly into the heaters from the so-called boiler manifolds. A third battery of reciprocating pumps took the water, now at a temperature of 330° F., from the bottom of the heaters to a line leading to one of the wells.

The boilers were 150 hp. horizontal return tubular type set in batteries of 8, 10, or 12. Two of these batteries were used in each steam plant and were separated by a small bay containing the boiler feed pumps.

Although some boiler compounds were experimented with, no effective water treatment was used, therefore the scaling problem was a major one in boilers, in lines and fittings, and particularly in the vertical contact heaters. These were cleaned regularly in constant rotation by removing the head, fishing out the trays one by one, and removing the scale by hand. In later years, prior to 1925, long chains coiled into the heaters were substituted for the trays; these constituted a forerunner of modern packed towers. The chains were dragged out and the scale flushed out of the heaters. Still later it was found that two or three trays at intervals in the heater, successively breaking the water into droplets, were almost as effective as a full complement of either trays or chain. During particularly dry seasons, the Houston River became brackish, and the water was used only to feed the heaters. Boiler water was provided from wells. Corrosion was particularly severe during these times and a crew was kept busy applying clamps to corroded spots in the hot water lines to the sulfur wells.

Controls and instruments considered necessities in a modern plant were missing. No meters were used and volumes of water were calculated, if at all, from rough estimates of the average number of strokes of the pumps. In fact, conventional stem thermometers and two or three pressure gages, besides the regular boiler gages, constituted the instrumentation. Insulation, where

used at all, consisted largely of burlap bags wrapped and tied on the hot lines and later of cellular insulation wrapped with tar paper.

Modern Techniques. The heating plant of a modern mine is usually a single central station supplying water for all wells. Watertube, gas-fired boilers and turbine-driven centrifugal pumps are used together with efficient insulating materials and accurate recording and control equipment. The two principal improvements, as practiced by Duval, over the old Union Sulphur plants have been in waste heat recovery and in removal of scale-forming solids from the water.

At Orchard all water is supplied by a group of 10 wells fitted with deep-well pumps driven by electric motors. In the summer the water is pumped into a 10,000,000-gallon dirt reservoir where it picks up solar heat with a resulting temperature increase of as much as 8° F. In the cold months the water (average temperature 72° to 74° F.) goes directly from the wells to the heating plant.

All water handling in the heating plant (Figure 1) is by steam turbine-driven centrifugal pumps in five steps:

1. Feeding cold water to the flue gas economizer
2. Taking suction from the economizer and feeding a battery of hot lime-soda softeners
3. Through calcite filters, then pumping to the boilers and mine heaters
4. Boosting the pressure of heated water received from the mine heaters at 125 pounds per square inch gage pressure and 326° F. to 250 pounds and feeding it into the field lines
5. Boosting a portion of the 250-pound water to a pressure of 400 to 600 pounds as may be required for special well-operating problems

The heating plant at Orchard Dome actually consists of the original Duval plant plus an additional plant moved to Orchard from Duval's operations at the Boling Dome. Since the principal function of a Frasch process power plant is the heating of water from ambient temperature to about 326° F., any heat available at temperatures above approximately 80° F. can readily be used. The greatest single heat loss in the early plants was in stack gases,

TABLE I. COMPARISON OF SULFUR WELL CONSTRUCTION

	PIPE STRINGS		Purpose
	Mine		
	Union Sulphur	Duval	
	12-inch	8-inch	Casing to top of cap rock to case off water sands and other alluvial beds
	10-inch and 8-inch	Liner pipe through to bottom of sulfur formation to conduct hot water into upper part of formation
	5-inch	6- or 7-inch (perforated for 15 feet in lowest part of formation)	To discharge hot water at a point near bottom of formation
	3-inch	3-inch	Tubing, reaching practically to well bottom, to conduct sulfur to surface
	1-inch	1-inch	Air line hung in 3-inch tube to introduce compressed air for airlifting sulfur to surface
HOT WATER LINES			
	Union Sulphur		Duval
Lines	One 4-inch, one 6-inch for each well; water pressure varied by operator according to well demands		One 12-inch (300 pounds per square inch working pressure) for 250-pound booster water One 8-inch, one 6-inch (both 600 pounds per square inch working pressure) for 250- to 600-pound booster water
Insulation	Pipes carried in continuous wooden troughs lined with tar paper and filled with sawdust		Welded steel lines insulated with sponge felt and wrapped with thin galvanized sheet for waterproofing

but with the advent of natural gas as a fuel, recovery of most of this heat became a very simple problem. In the Orchard unit approximately 75% of the flue gases are passed upward through an economizer (a steel shell 10 × 17 × 30 feet, open at the top) against the downward spray of the entire volume of fresh water entering the Orchard unit system (1800 gallons per minute), introduced through three sets of spray nozzles (2E) near the top of the economizer (Figure 2). Flue gas temperature is thus reduced from about 550° to approximately 90° F., the gas is exhausted to the atmosphere, and the water leaves the economizer at 104° to 112° F. depending on seasonal variation of the temperature of the water from reservoir or water wells. From the economizer the water is fed to the treating system. No economizer is operated with the Boling unit at present, although consideration is being given to a future installation to take advantage of the Boling waste heat plus the 25% of the Orchard flue gases which are exhausted direct to the atmosphere through stack fans because of the limited capacity of the Orchard economizer. The only undesirable products picked up from the flue gases are carbon dioxide and oxygen, both of which are driven out of solution and bled off almost immediately in the lime-soda softeners. Instead of open towers some plants use packed towers.

Introduction of efficient water treatment has been an improvement even more important than heat recovery; without it the use of centrifugal pumps and other modern plant equipment and use of long permanent water lines to the field would be impractical because of scaling. The Duval plant uses a hot lime-soda process (4E), in which 1800 gallons of water per minute from the economizer enter the two softeners of the Orchard unit and 1000 gallons per minute of water direct from the reservoir or wells enter the Boling softeners. Capacity of the Orchard softeners is 60,000 gallons per hour each and that of the Boling 50,000. Figure 3 shows a cross section of the flow through one of the Orchard unit softeners. In these softeners the temperature of the water is raised to approximately 218° F. This is accomplished in the Orchard group largely through the use of exhaust steam, with the addition of a small quantity of live steam. In the case of the Boling unit, however, not only is the temperature of the entering water lower, but the unit has no compressors and turbogenerators and consequently little exhaust steam. Live steam alone, then, is fed to the Boling softeners.

Duval has four lime solution tanks, a fifth as an auxiliary, and one soda ash tank. Milk of lime is pumped to the softeners at a ratio of 2.2 pounds per 1000 gallons of water and soda ash at 0.1 pound. Because of the silica content of the raw water it has been found necessary to add magnesium oxide in the ratio of 0.23 part per 1 part of lime.

Operating in the conventional manner as described by Butterworth (3), who gives a detailed description of a somewhat similar lime-soda process and the chemistry involved, Duval engineers found that the turbidity of the treated water was still about 50 to 150 p.p.m. The difficulty has been solved in their process by recirculating in a closed circuit with the softener a portion (30 to 80 gallons per minute) of the sludge formed in the cone-shaped settling bottom of each softener. A part of the sludge is also added to the lime feed to keep the lime solution lines open. The sludge "blanket" provides nuclei for growth of the newly precipitated calcium carbonate and reduces turbidity to approximately 2 to 10 p.p.m.

Continuous desludging also takes place from the bottom of the softeners at a rate, determined by the thickness of sludge, needed for best clarification (approximately 6 gallons per minute for each softener), and each treater is completely desludged (approximately 2800 gallons) each day.

From the treaters the water passes through calcite filters. The Orchard unit has five horizontal filters (0.55 square foot of filter area per gallon of water per minute, and the Boling unit has six vertical filters (0.30 square foot). These latter filters have been found to be more satisfactory than the horizontal

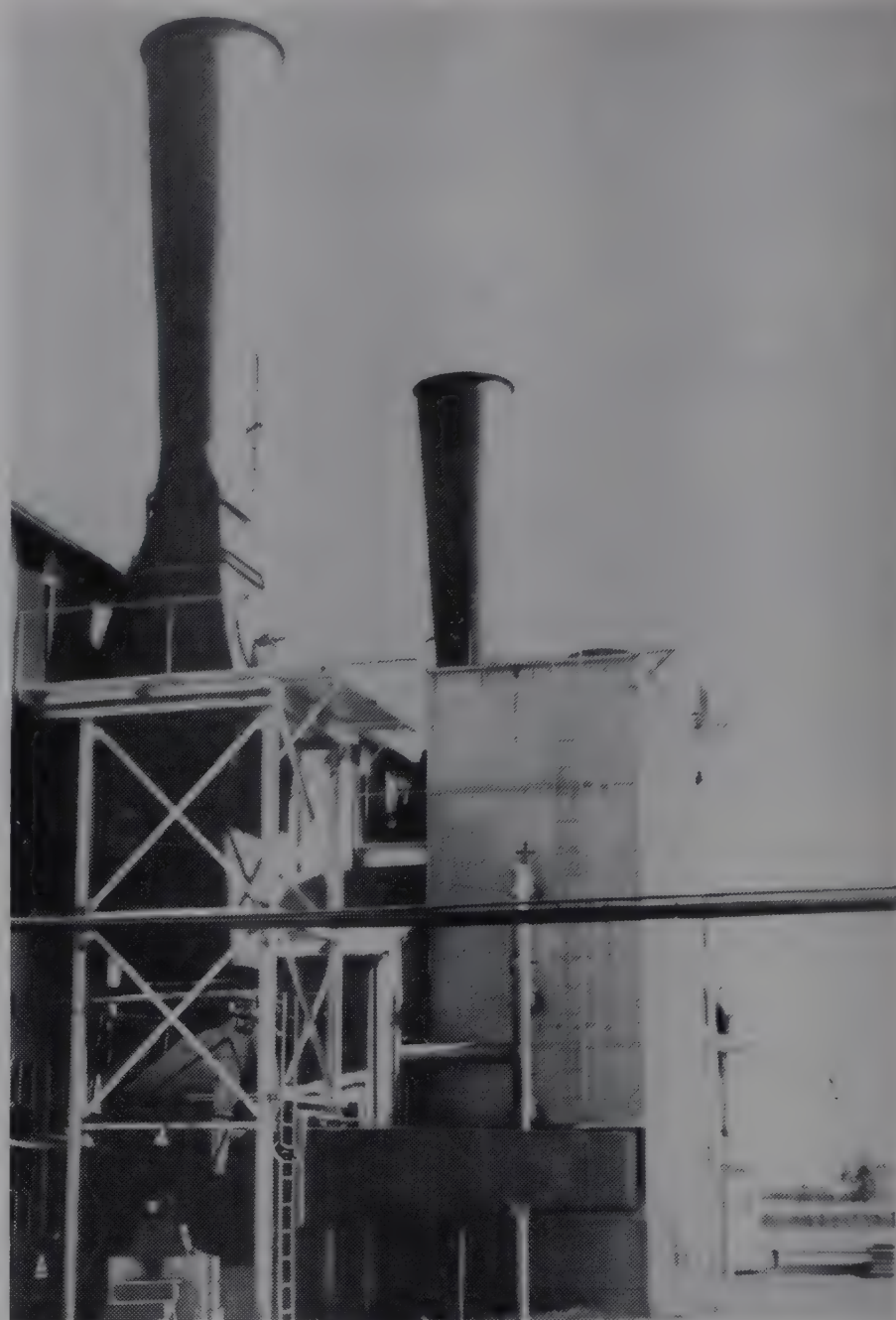
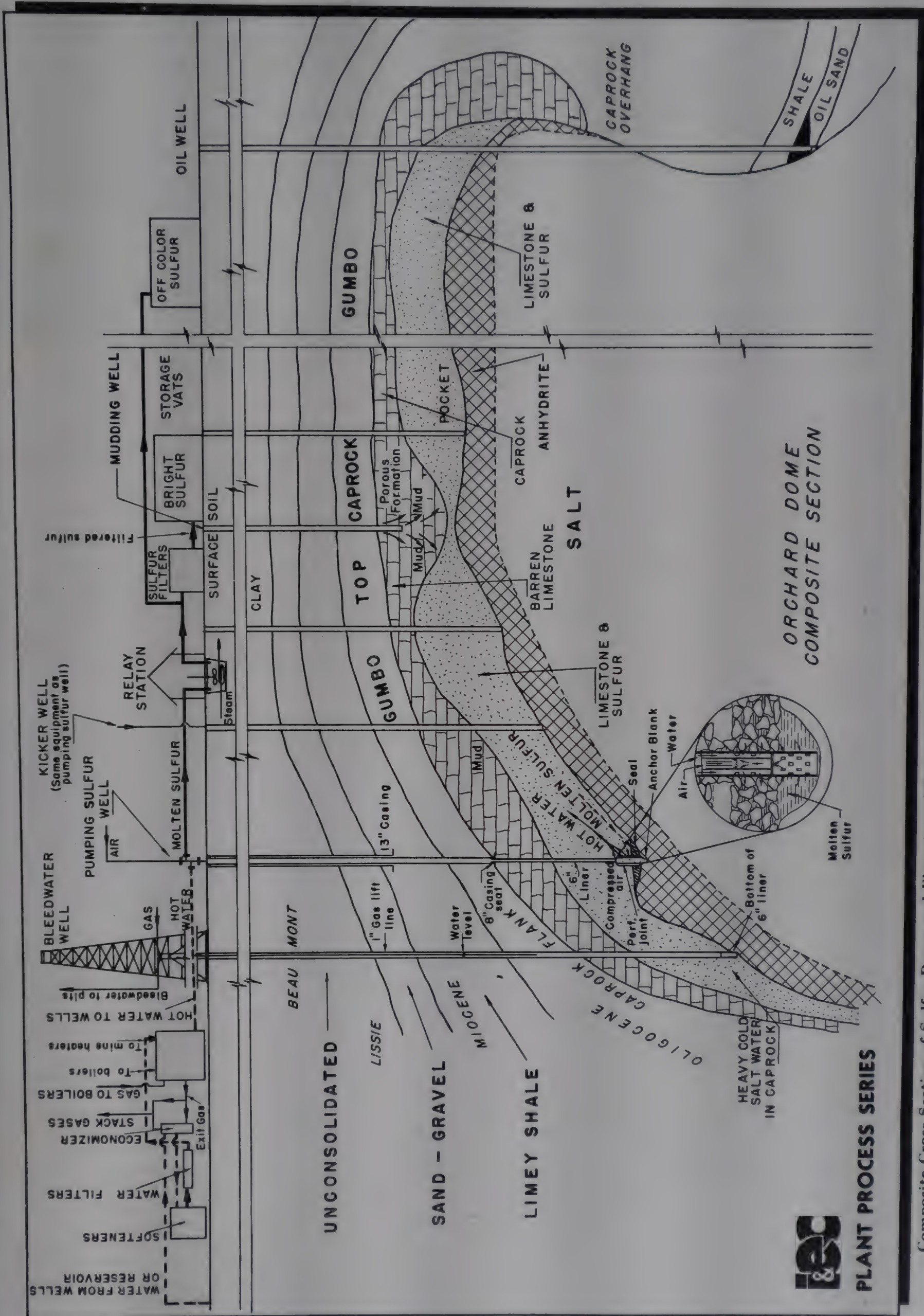


Figure 2. Economizer

type, because of greater efficiency and less tendency toward mudball formation and channeling. Leaving the filters the water has an average residual hardness of about 5 p.p.m. and zero turbidity.

A portion (approximately 17%) of the treated water goes to the boilers for generation of 125-pound steam, and the rest goes to the mine heaters. The Orchard unit has four 700-hp. and the Boling unit four 500-hp. boilers. These are four- and three-drum, respectively, bent-tube watertube types mounted in batteries of two, with a Venturi-type stack and a steam turbine- or electric-driven fan used for each battery. As contrasted with the 1000- and 1500-hp. boilers used at larger and more permanent mines, Duval's 500-hp. boilers can be moved in one piece, and the 700-hp. boiler units require only partial dismantling. Natural gas is normally used as fuel. Oil burners are ready for immediate use should the gas supply be interrupted, and the switch to oil fuel can be made through the entire plant in about 10 minutes. It is interesting to note that in contrast, the largest producer in this country, Texas Gulf Sulphur Company, because of the expected long life of its deposits at Newgulf, Tex., designed the boiler settings in the heating plant there to permit installation of lignite-burning equipment in the event that depletion of natural gas supplies seemed imminent or prices should favor the use of lignite, which is plentiful in Texas.

The mine heaters (Figure 4) are fed live steam direct from the boiler header and 218° F. water from the boiler feed pumps. They are relatively small as can be seen in Figure 4 by comparing them with the water feed lines; the dome part of the mine heater where heating is accomplished is 3 feet in diameter by 5 feet high. The heaters are actually steam condensers (open-type rather than jet) through which pass approximately 125,000,000 gallons of water per month.



Composite Cross Section of Sulfur Dome and Elevation of Processing Plant at Mine of Duval Sulphur and Potash Company, Orchard Dome, Texas

The mine heater discharge water goes to the low pressure booster pumps, where pressure is raised to 200 to 300 pounds per square inch. For higher pressures, as needed by the operators in the field, rebooster pumps may bring it to 300 to 400 pounds per square inch, or the water may go directly from the mine heaters to the high pressure pumps where 600 pounds per square inch are attained.

The heating plant building proper, constructed with structural steel frame, galvanized corrugated steel walls, and concrete floors houses all the principal equipment except the economizer, the fuel oil storage and pumps, and the water-treating equipment. Water-treating tanks and filters are in the open, protected by magnesia block insulation waterproofed with a bituminous covering. Mixing tanks, sludge feed pumps, and filter backwash pumps are housed in a separate building with stored chemicals. All plant buildings are of the same design and are constructed in units so that they can easily be enlarged or dismantled. All hot surfaces are insulated; the materials vary from light cellular asbestos on low temperature lines to 2-inch magnesia and sponge felt on steam and hot water lines.

Recording pressure gages, thermometers, and flowmeters keep operators informed at all times of equipment performance. Water flow from the final booster pump to the field is controlled manually by the operators.

FIELD OPERATIONS

In field production techniques we find an even greater contrast between the old and the new. At the old Union Sulphur Company mine heated water was piped from each plant to its particular well in two lines; at Orchard there are three lines from the central heating station to the field. Comparisons are shown in Table I. Relay stations in the Orchard field, equipped with indicating orifice meters, are used to proportion the water to the various steaming wells.

The procedure for operating the wells is little changed from that devised by Frasch except that no hot water is introduced high in the formation as was done in Union Sulphur's operations. Present-day techniques of introducing all the water near the bottom of the well tend to increase the volume of formation included within the sulfur drainage cone by (a) increasing the altitude of the cone in respect to the bulk of the water and (b) increasing the pressure of the water entering the formation at the bottom and thus forcing the hot water out at a flatter angle into the formation.

After the sulfur-air entrained mixture reaches the top of the 3-inch tubing in the well, however, its handling is quite different from the early practice. When a Union Sulphur Company well was pumping, this mixture was conducted through 4-inch lines directly from the wells to the storage vats. These discharge lines were carried on wooden trestles with a continuous upward slope to the point of discharge, so that they could be drained back to the wellhead when pumping ceased, to prevent freezing. Figure 5 is a photo, previously unpublished, of these trestles; the stacks of three individual heating plants appear in the background. At the vat discharge the air escaped and liquid sulfur spread out in thin layers and solidified.

At Orchard the entrained mixture from a particular well is conducted to that well's relay station through 4-inch lines; these lines are not only insulated but also have 1-inch steam or gut lines in them to eliminate freezing. With freezing dangers thus avoided the trestles are not necessary, and the lines are simply laid on blocks on the ground. At the relay station the entrained mixture discharges discontinuously directly into a steel pan (60 to 100 tons capacity) sunk into the ground, air escapes into the atmosphere, and sulfur collects as a liquid in the pan which has steam coils in the bottom. (Larger operators also line the sides of their relay pans with steam coils.) When sulfur is not being pumped from the well, cross connections at the relay station are employed to flow hot water back through the 4-inch sulfur line and down the 3-inch tubing into the well. Other operators (23) pass the entrained mixture through a separator as soon as it

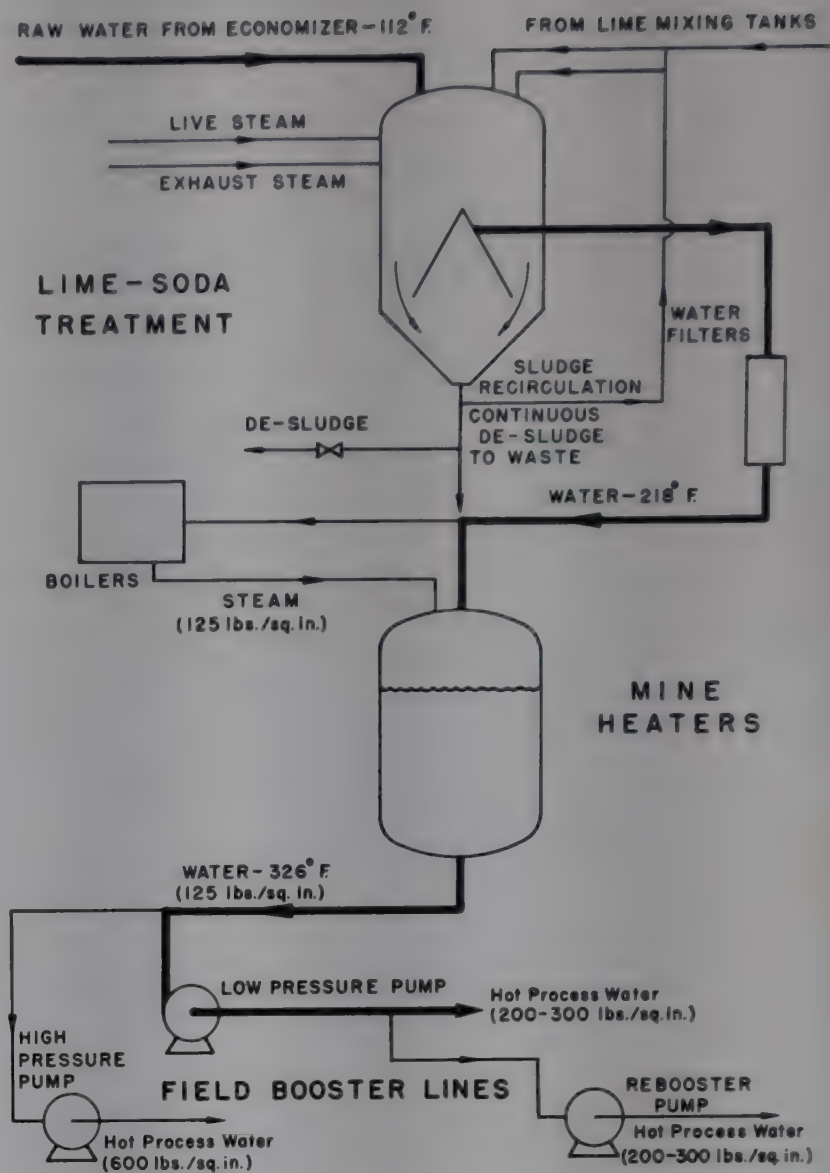


Figure 3. Flow through Water-Treating Plant and Mine Heaters

comes from the well; the withdrawal of air from the molten sulfur in the separation chamber is controlled at a rate to maintain adequate pressure to force the sulfur from the chamber to the relay pans. Main advantages of this refinement to the collecting process, besides giving a more continuous flow of liquid sulfur, are minimized corrosion and virtual elimination of the sulfur vapor nuisance around the relay station. Duval has found that in its operations the advantages thus gained are not sufficient to justify the expense of the separating equipment, particularly since the conditions under which it operates are not as corrosive as those of some other sulfur miners. Hackerman (7) discusses in detail the corrosion of steel in sulfur producing lines.

Vertical motor-driven steam-jacketed centrifugal pumps periodically empty the relay pans, delivering the sulfur through steam heated lines to the vats. Here again steam gut lines mounted in the sulfur lines make it unnecessary to drain the vat discharge lines, and they are laid on blocks, following the most advantageous route. An additional advantage of collecting the sulfur in relay pans and relifting it to the vats is that the vats can be located permanently at any desirable point.

COOLING AND STORAGE

Old-style vats for sulfur storage were built up of form lumber and were similar to concrete forms, except that they were supported from the inside by 1 × 4's imbedded in the sulfur itself. Completed vats were 100 to 200 feet wide, about 30 feet high, and several hundred feet long. For some years the fire risk was considered too serious to justify the use of dynamite for shooting down the sulfur in the vats for loading out, and it was done by hand with crowbars and picks; freight cars were then loaded from wheelbarrows.

Very little of the form lumber used in the old vats was suitable for use a second time and the nails and lumber left in the completed vats were a source of trouble. Through the years many attempts have been made to solidify sulfur in usable form without pouring it into a solid block or vat, but none was commercially

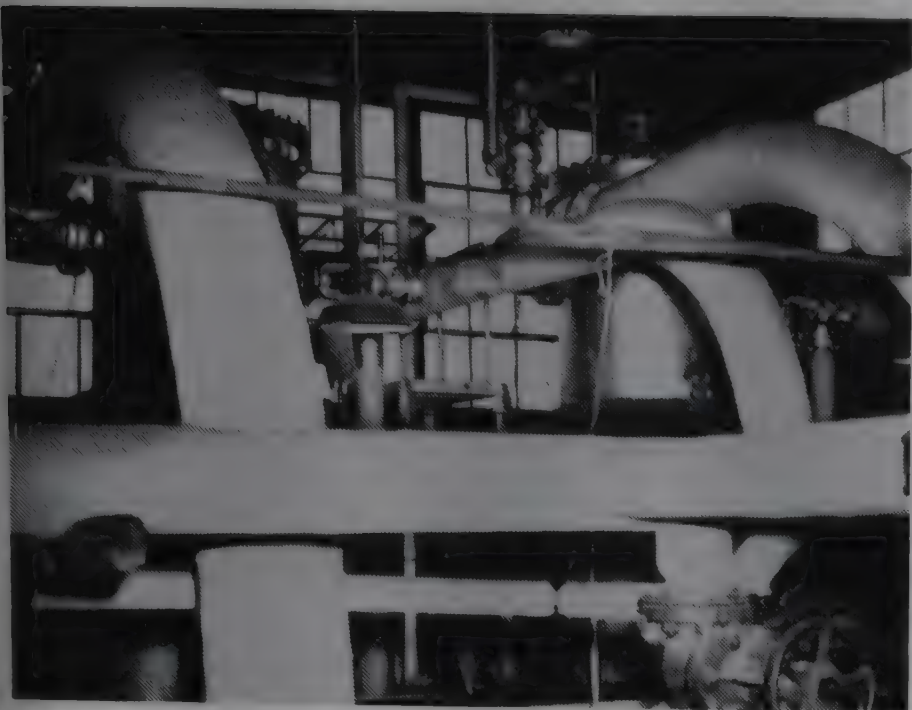


Figure 4. Mine Heaters

successful. Finally, some vats were formed with flat galvanized metal sheets in place of the shiplap and these sheets, if the edges were reinforced with light angle iron, could be removed readily and most of them could be reused. This proved to be rather untidy looking, since the flat sheets bulged from the liquid head of the sulfur inside the vat and from the unequal expansion strains due to successive heating and cooling.

Sulfur vats cannot be filled too fast because if the vat forms a "surface crust," more sulfur, if added to the vat top, solidifies, leaving an insulated pocket of hot liquid sulfur which will remain liquid for a long time due to the high insulating value of solidified sulfur. This hot spot in the vat could be dangerous to the workers around the vat when it is dynamited prior to shipment.

The method finally and successfully used at Orchard involves corrugated metal sheets for forms; these are moved up tier by tier as the vat level is raised. The galvanized corrugated sheets are nailed to 2 × 4 uprights which are on the inside of the vat wall and are held in place by the sulfur on three sides. Double-headed nails are used and special nail pullers are employed which can be operated by men standing on the solidified vat surface and reaching down over its side. When the sulfur level is a few inches above the top of a given tier of corrugated sheets, that tier is removed, pulled up on the vat, and re-erected to form a higher tier. Two tiers are continuously used, leapfrogging one over the other, and when a vat is finished the last tier is removed. Thus no nails or other metal, but only the wooden uprights remain in the sulfur.

A further advance in vat construction (30) has been made by the Texas Gulf Sulphur Company at Newgulf, where the vat walls are formed tier by tier out of sulfur itself, using aluminum forms which are removed before the level of the vat sulfur reaches them. The resulting vat thus contains no materials of construction whatsoever. Texas Gulf has also patented a method (31) for continuously forming shot holes for blasting the vats.

The Freeport Sulphur Company at their Grande Ecaille, La., operations uses another recent development in vat handling. This method eliminates dynamiting completely by the use of lower vats and steam shovels for loading from the vats into conveyors or cars.

At Orchard the completed vats are shot with dynamite loaded in shot holes drilled from the top of the vat with a miniature rotary rig similar to a regular well-drilling rig. The shots, with the heaviest load near the ground level, shatter the top and kick the bottom out, thus permitting the top to fall. Sulfur is fairly friable and the resulting breakage is usually sufficient for handling. Locomotive cranes using clamshell buckets load the broken sulfur into rail cars. Shipments of liquid sulfur to local customers are made by some producers in heated tank cars. When customers use sulfur as a liquid theoretically the shipper is saved the cost of

vat building, drilling, shooting, and loading, and the customer is saved the time and cost of remelting. However, disadvantages to the producer may outweigh the advantages. These disadvantages lie chiefly in the fact that if large tonnages of molten sulfur are moved, adequate provision must be made to maintain the material in liquid form; also elaborate loading racks are necessary to avoid excessive locomotive costs due to spotting cars. On the basis of occasional tank car shipments it is questionable whether extra handling costs do not wipe out any theoretical savings.

SPECIAL PROBLEMS

Bleedwater Recovery. Day after day an immense quantity of water is pumped into a sulfur deposit and only a relatively small quantity of sulfur is removed. The sulfur formation at times is more porous than the barren limestone cap rock. A small amount of the excess water finds its way up through the cap rock and out into sands in contact with the top of the cap. Some displaces colder, heavier water which is pushed down around the flanks of the dome and leaks off into lower sands. If the dome pressure is allowed to increase, some small part may make room for itself by compressing pockets of gas sometimes found in the caprock. None of these outlets, however, ordinarily accounts for more than a small fraction of the input water, and some means must therefore be provided for removing large volumes of cold cap rock water to make room for the hot mine water and to prevent difficulties due to greatly increased pressures in the dome.

TABLE II. TYPICAL BLEEDWATER ANALYSIS^a—ORCHARD DOME

	P.P.M.	Grains/Gallon
Silica (as SiO ₂)	21	1.2
Fe ₂ O ₃ and Al ₂ O ₃	10	0.6
Ca	501	29.3
Mg	21	1.2
Na	37,600	2195.0
Bicarbonate	278	16.2
Sulfate	1,120	65.5
Chloride	57,900	3380.0
Hydrogen sulfide	Present but not determined	

^a pH 6.9 to 7.1.

At Orchard the mine water is removed by equipping wells around the edges of the mining area with eduction strings of pipe reaching to a deep cold zone. The cold, heavy cap rock water is allowed to flow, if it will, but is usually pumped from these bleed wells. The bleedwater, dark green in color and containing a varying quantity of salt up to saturation, is not useful and consequently poses a disposal problem (Table II gives an analysis typical of bleedwater at Orchard). Frasci solved his bleedwater problems by building a narrow reservoir about 1.5 miles long and 500 feet wide; here he impounded bleedwater during dry seasons and flushed it into salt water bayous during high water periods. Duval also employs the impounding technique, but generally has no emptying problem. Two impounding reservoirs have been built with sufficient surface area (150 acres each) exposed so that evaporation is equal to input over long periods of time.

A second method for disposal of bleedwater consists of treating it to remove constituents, such as hydrogen sulfide, which are harmful to animal life and then emptying it into surface water drainage areas. This technique is practiced by the Texas Gulf Sulphur Company. Aeration, with addition of chemical catalysts, was practiced for a number of years to remove the harmful constituents, but Texas Gulf's present installation (3) includes a unit design to drive off the soluble sulfides by passing the water through a packed tower countercurrent to a flow of flue gas and to reduce corrosion problems by chemical treatment. After treatment the bleedwater is piped about 20 miles to tidewater.

Some operations require bleeding of large quantities of relatively hot bleedwater and disposal of such bleedwater would result in the loss of great quantities of otherwise recoverable heat. The most effective use of bleedwater heat has been made by the Freeport Sulphur Company (19) at its Hoskins Mound, Tex., mine. Originally this bleedwater, at 220° to 250° F., was com-

bined under pressure with water at 355° F. from the mine heaters to produce water of the proper temperature for injecting into the mines. More recently it has been found practicable to condense high pressure steam into the water in a suitable pressure vessel, allowing the use of 90% recovered bleedwater in mining operations. This water is acidic (pH approximately 6.5) and is very corrosive when hot (above 90° F.). In order that it can be re-used without excessive equipment destruction, Freeport Sulphur Company developed a chemical technique involving treatment with hydrated lime and an alkaline phosphate-barium chloride. This treatment results in the deposition of a layer of insoluble scale on the equipment and water-carrying lines, thereby sealing metal surfaces against the corrosive water.

Voids and Subsidence. As a result of the removal of large volumes of cap rock structure in the form of liquid sulfur, voids and cavities are left. These sometimes become troublesome to a producer in two entirely different ways.

The bulk of a stream of hot water entering a mine will follow the most open channels, with a relatively smaller amount seeping through smaller openings into new rock. Thus the more sulfur a particular block of cap rock has given up, the greater the tendency of the water to flow through that block, whereas formation that is still virgin restricts the flow of hot water. Frasch did some partially successful experimenting toward blocking these voids; other mines have found the problem more vexing than he did and have tried several remedies. The one which has proved most satisfactory and is in use at Orchard was developed largely by the Freeport Sulphur Company at its Hoskins Mound mine. This consists of pumping large quantities of mud into the cavernous formations, through wells. The success of this method is due to the fact that wherever the cavities traversed by the mud are large, the velocity is decreased and the solid particles in the mud settle out, tending to fill the voids. Where porosity is small, velocity of the mud is high and the solid particles are swept through. Size of the solid particles can be varied to suit local conditions and selection of wells for mudding is flexible. For example, sometimes a row of adjacent wells will be mudded to form a continuous barrier across a certain section. Other controlled variables are the depth of discharge of the mud, the percentage and character of the solid particles in the mud, and rate of pumping the mud stream into the well; all factors are generally determined by the way the well takes the mud.

Ordinary clay mud is dumped by dragline into a two-stage paddle-type mixer, in which the paddles accomplish some grinding while mixing the mud to a clayball, clabber consistency. Four slurry pumps (3E), 500 yards per hour rated capacity, are used to pump the mud into the wells.

The second problem arises from the same source (removal of one constituent of the caprock structure as liquid sulfur), and occurs when the remaining skeleton formation does not support the weight of the formations above it, but instead is crushed down and compacted. When this happens the underground voids are filled and any necessity for mudding is eliminated. Solution of this one serious difficulty, however, introduces several new ones. When the settling occurs, it is apt to distort and frequently break the strings of pipe in the wells. The only defense against this is to drill and equip the wells only as needed and, where advisable, to replace lost wells with new ones.

If the settling is extensive, it will eventually show up on the surface of the ground and is referred to as subsidence. In such cases it may affect pipe lines, roads, and drainage. In flat coastal country subsidence areas will soon become ponds if not pumped out; pipe lines that were originally horizontal will be elongated or parted by dipping down through the depressions; and derricks and other structures will be thrown off-level. At Orchard the surface subsidence problem has been negligible, but it has been marked at the Newgulf mine of the Texas Gulf Sulphur Company, where considerable vertical movement has been noted. The subsidence problem has been handled in two ways in various locations: Either the depressions have been isolated from surface drainage and kept pumped dry of rain water, or they have been

TABLE III. FILTRATION PROCESS

Steps	Remarks
Direct filtration	Initial operation only
1. Crude sulfur from relay station to 100-ton first-stage pan	Clay builds up cake on filter for two-stage filtration
2. Mixed with clay in sulfur-jet mixer and back to pan	
3. Through filters to bright pan	
4. Bright pan discharged to storage vat	
5. Filter cake ready for two-stage filtration or discarded	
Two-stage filtration	Routine operation
1. Crude sulfur from relay station to 100-ton crude receiving pan	Pans also used as cake-dropping pan in later steps
2. Through cake on filters and into second-stage or cake-building pan; additional clay added to this pan	Two pans available: one 100-ton pan for crude or for cake-building sulfur; one 50-ton pan for cake-building sulfur only
3. When cake is exhausted, filters are emptied back into cake-dropping crude pan	Exhausted cake dropped after each two-stage cycle and filter opened at end of 5 cycles or about once each shift; two tons cake-dropping sulfur emptied each time filter is opened
4. Cake is dropped	Discard
5. Sulfur-clay mix from second-stage pan through filters to bright pan	To build up cake
6. Bright pan discharged to storage vat	
7. Filter cake formed and ready to receive crude sulfur again	

progressively filled with dirt to maintain approximately their original level. In either case adjustment of lines, ditches, structures, and roads is made to match the changing surface level. One important point that should be brought out in the subsidence problem is that power plants, storage vats, and other permanent structures should, if possible, be constructed at points beyond the limits of any possible surface subsidence area.

Contamination. Two problems of contamination may be involved in sulfur mining—entrained solids and/or adsorbed impurities. Normally, production of liquid sulfur from wells results in very little entrainment of solid particles, but on occasion some calcareous or gypsiferous sands from the caprock or siliceous sands from above the cap work their way to the bottom of a well and are entrained by the liquid sulfur.

At the Frasch mine any such entrained solids were pumped onto the vat and remained as impurities in the sulfur after it solidified. Production today includes "blowing" a well into a waste or blow box immediately when the well ceases to pump sulfur. The procedure involves short-circuiting the hot water going down the strainer string of pipe through the sulfur bowl at the bottom of the well and back up the tubing, then blowing it into the open blow box. The rate of flow of this hot water is much greater than that of the flowing sulfur and it therefore to some extent washes the bowl and cleans out at least a portion of any sands that may have collected.

More important, any sands that are brought to the surface in the liquid sulfur are settled out in the relay pans before the sulfur is pumped to the vats. In modern sulfur mining, consequently, there is practically no contamination due to entrained solids.

The sulfur produced from salt domes of the Gulf Coast is very pure and is notably free of arsenic and selenium. Bacon and Fanelli (1) list the small amount of impurities present as moisture, acid, dirt, dissolved and absorbed gases, and organic matter. The latter, which it may be necessary to remove for some uses of sulfur, are probably compounds of, or including, sulfur and carbon or possibly hydrocarbons. They are black in color and small percentages will stain the sulfur so that when solidified it assumes shades grading from brownish yellow to black. A total content of 1% of such carbonaceous impurities will impart to the solidified sulfur a color approaching that of bituminous coal.

Two successful methods have been used for substantially eliminating the carbonaceous type of impurity. At Orchard the sulfur is relatively off-color when stored directly as it comes from the relay pan. Although this sulfur is satisfactory for a large number of Duval's customers, it is necessary to decolorize it further for others. The method used at Orchard involves treatment of liquid sulfur with a specially prepared clay product (1E) which

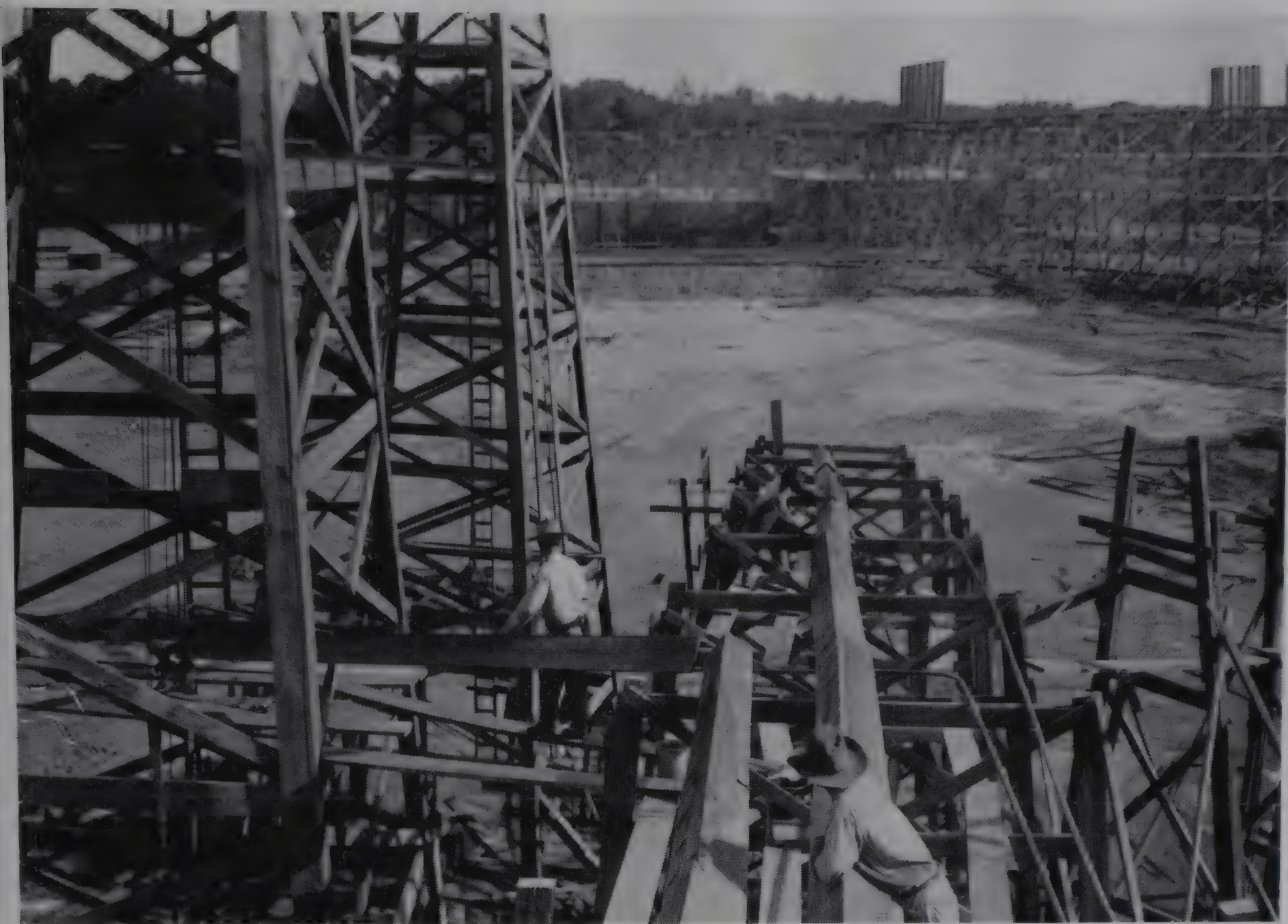


Figure 5. In Early Days of the Sulfur Industry Wooden Trestles Supported Lines Carrying Sulfur from Mine to Storage Bin

has a selective affinity for the carbonaceous impurity. This impurity is adsorbed by the clay particles, and the clay is then filtered out on metal screens in a pressure filter designed by Duval engineers. Texas Gulf Sulphur Company uses a somewhat different filtration process (one-stage) and a screen (25) designed by its own engineers. The Duval technique is quite effective, and the resulting product contains a negligible amount of impurities. The cost of treatment varies with the percentage of impurities and is represented principally by the amount of clay used (governed by the fundamental Freundlich adsorption equation) and the cost of labor.

The diagram of flow of the crude sulfur through the filtration process is illustrated in Figure 6, and Figure 7 shows one of the filters in operation. At the beginning of operations the process is direct, as contrasted with the two-stage filtration practiced in routine operation. Steps in carrying out both operations are shown in Table III. In two-stage filtration, the "cake-dropping" sulfur is discharged into a separate pan and treated with additional clay because experience has shown that most efficient filtration occurs when crude and partially purified sulfur are not mixed.

At another mine, where the percentage of carbonaceous impurities is higher and filtration would be too costly, the sulfur is vaporized (17), using a gas-fired watertube type boiler and draining the impurities off from the mud drum when they are sufficiently concentrated. The vaporized sulfur is condensed in surface condensers and heat exchangers where the heat of the condensate is transferred to the crude liquid sulfur fed to the boiler.

Hills (11) has patented a purification technique in which molten sulfur is mixed with chlorosulfonic acid and a filter aid; the filter aid and impurities are then filtered off, but this technique is not

being used at present in the industry. As a matter of interest it might be mentioned that some years ago a method was patented in Germany (15) for removing organic constituents from sulfur by treating it in a molten state with gases containing ozone.

LABORATORY TESTS

The main functions of the chemical laboratory at Orchard and in general at other mines are assaying and testing and analyzing in connection with water treating. In the field of sulfur analysis, however, Duval's laboratory runs analyses of the cores on each test well, determining the percentage of sulfur by extraction with carbon bisulfide; once each month the sulfur produced is analyzed for organic matter and ash. Every batch of sulfur discharged onto the vats is sampled, a composite is made over an 8- to 10-day period, and analysis is carried out for organic matter and ash. In this analysis Duval utilizes the free-burning method, adding a little purified sulfur. Carbon is then burned off and ash determined by difference. All color examinations of finished sulfur are visual, since visual examination has proved consistently accurate and is satisfactory to Duval's customers.

UTILITIES

Natural gas for the Duval operations is obtained from wells of the Gulf Production Company, 2000 to 4000 feet from the heating plant. Because low pressure steam can be used at good efficiency, electric power can be generated at costs below those of utility companies. At Orchard two 500-kilowatt steam turbine-driven 2400-volt alternating current generators furnish power for lighting, sulfur pumping, water wells, repair shops, vat drilling, and all other mine requirements (Table IV). Average daily usage of utilities for the entire plant (Orchard and Boling units combined), based on the first 6 months of 1950, is:

Gas, millions of cubic feet	9.9
Water (process only), millions of gallons	3.9
Electricity, kilowatt hours	8025

FUTURE PROSPECTS

The problem presented by approaching exhaustion of minable sources of sulfur in this country has had considerable attention recently. Detailed reviews of the world sulfur industry have been given by Duecker (6), Mathews (22), Thame (27), and Lundy (18). Josephson (12), reviewing the industry as of 5 years ago, pointed out the improvement of gas treatment methods and the increase in that type installation. Satisfactory methods for the conversion of hydrogen sulfide from sour and refinery gases are in operation in Wyoming, New Jersey, Arkansas, and California. Hader and Herndon (8) describe one of the sour gas installations in the following chapter of this book. Hydrogen sulfide sources and processes for utilizing the gas to obtain commercial sulfur, production of sulfur from sulfur dioxide in metallurgical processes and removal of sulfur compounds from gas streams by hypersorption are all discussed in this symposium. Khmenko (14) in Russia has patented a method for burning sulfur directly underground and collecting sulfur dioxide at the surface.

Agreement appears general in the industry that surface processing equipment used in the Frasch Process has been developed to about the peak of its efficiency and that only much deeper deposits or sulfur mining in the tidelands (28) will offer engineering challenges in the Frasch field. One of the difficulties that arises concerning sulfur developments in the tidelands is that the general tendency in tidelands drilling by the oil companies is to drill at the flank of the dome rather than at the top of the dome where sulfur is most likely to be found. Further, although leases covering oil and gas drilling in the tidelands of Louisiana include sulfur rights, those in Texas do not; it is assumed that government leases in like areas also do not cover sulfur rights. There are relatively few shallow domes in the tidelands areas; the percentage of these domes likely to have sulfur is small; and the sulfur mining companies alone cannot assume the heavy risk of tidelands prospecting. This is accentuated by two additional factors. First, the price of sulfur has been stable for many years, and a recent increase from \$16 to \$18 per long ton is simply a restoration of a drop that took place in 1937. The exploration and operation of any sulfur deposits under water in the tidelands would be entirely too expensive at the present price of sulfur. Secondly, with shallow domes sulfur prospecting would necessarily not go very deep, and therefore it would be uneconomical to build the huge rigs that must be built for tidelands oil domes. The lighter the rig, however, the more danger of its being damaged by storms, and the balancing of these factors presents a difficult economic problem.

Before the first World War pyrites were the chief source of sulfur. As native sulfur from the Gulf Coast gained a stronger economic foothold because of cutting off Spanish imports, and the use of sulfur for acid manufacture increased, pyrites began to lose ground. Domestic pyrite sulfur production in 1900 was 200,000 long tons; that of sulfur by the Frasch process was 7,382 long tons in 1903, 85,000 in 1904, and 220,000 in 1905 (24). Figure 8 shows strikingly the production curve of the two sources. Perhaps industry should have continued to use pyrites as a source of sulfur for many uses where arsenic- and selenium-free sulfur is not required. Nevertheless, it did not because of the availability of minable sulfur, as the figure clearly shows, and as a result the sulfur deposits as we know them could easily be exhausted in 25 years. At the present price of sulfur, of course, that from pyrites cannot economically compete with mined sulfur to any degree.

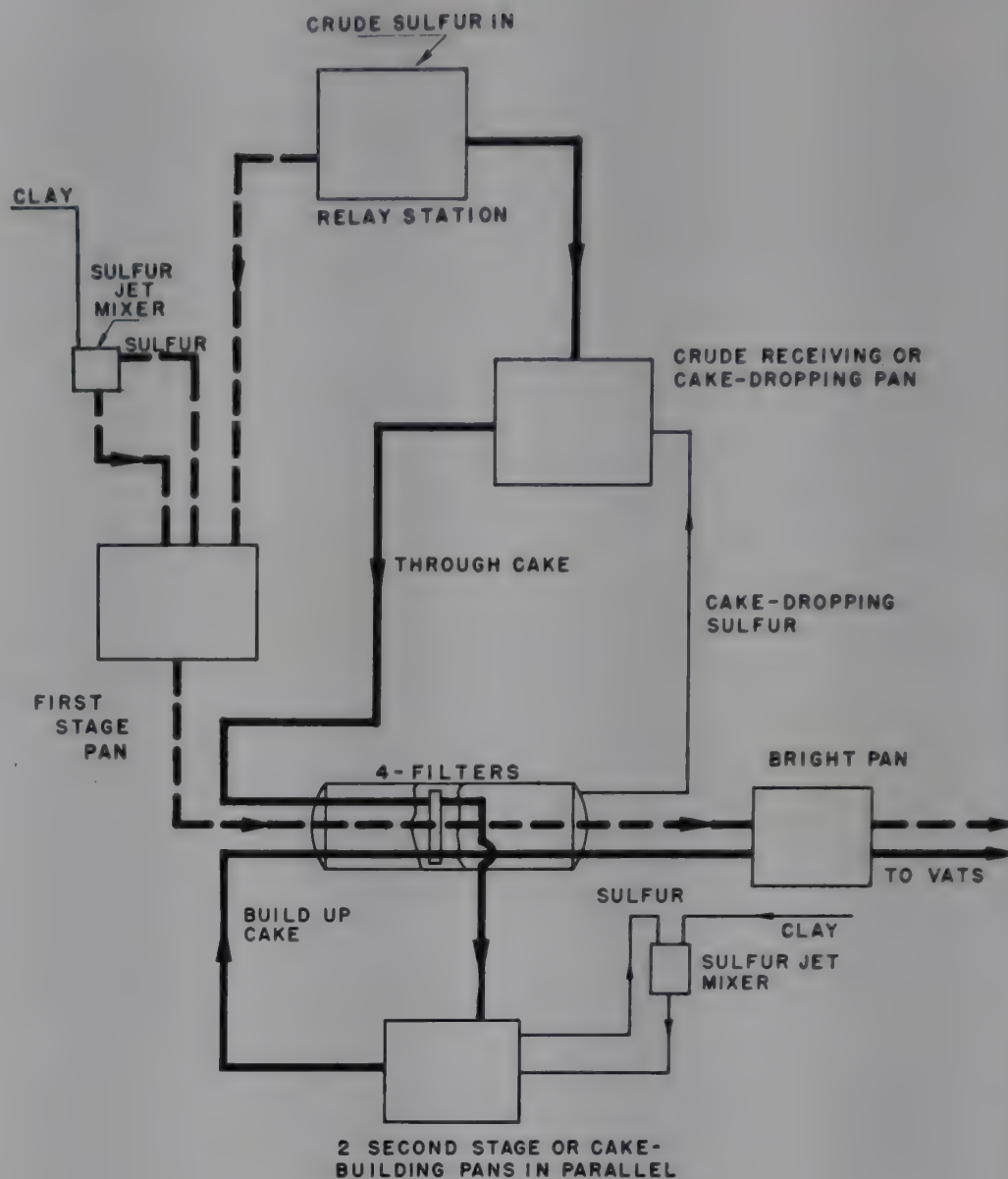


Figure 6. Flow of Sulfur through Filters

Some price adjustments may yet have to be made to improve the situation, and since the sulfur necessary as a raw material in present day industry cannot be supplied by gas sources (which are in themselves uncertain), industry will probably be forced to return to pyrites as a principal source. It is possible that if industry uses powdered coal to any extent it will be feasible to wash and screen out the "brasses" or lumps of pyrite which are found,



Figure 7. Sulfur Filter in Operation

TABLE IV. SUMMARY OF HEAT AND MATERIAL BALANCES

(Orchard unit only)

	Heat Balance (Gas, 60° F.; Water, 32° F.), B.t.u. × 10 ⁶	Material Balance, Millions of Pounds		Heat Balance (Gas, 60° F.; Water, 32° F.), B.t.u. × 10 ⁶	Material Balance, Millions of Pounds
ECONOMIZER (flue gas: inlet, 570° F., outlet, 90° F.; water: inlet, 77° F., outlet, 108° F.)			BOILERS (1 mole fuel = 10.98 moles dry flue gas)		
Heat in, from			Gas side		
Dry flue gas (75% of stack gases)	5.22	4.13	Heat in, from		
Water vapor	6.6	0.5	Fuel gas	71.3	0.52
Water	10.03	22.3	Heat out, in		
Heat out, in			Dry flue gas	7.87	5.83
Dry flue gas	0.3	4.13	Water vapor (25% of treated water)	6.6	0.5
Water vapor	1.41	0.1	Transferred	55.2	...
Water	17.25	22.7	Losses (radiation)	1.6	...
Losses (radiation)	2.89		Water side		
SOFTENERS			Heat in, from		
Heat in, from			Softener	11.8	6.8
Economizer	17.25	22.7	Gas side	55.2	...
Chemical treatment	0.01	0.08	Heat out, in		
Exhaust steam	4.03	0.38	Steam	63.5	5.78
Live steam regulator	29.4	2.46	Blowdown	3.47	1.02
Continuous blowdown	3.05	0.94	Losses (radiation)	1.6	...
Heat out, in			Waste through open stack (25% of total flue gases)	3.62	...
Effluent	48.8	26.6	Radiation, stack to economizer	0.68	...
Losses (radiation and precipitation)	5.03	0.12	AUXILIARIES (assumed 80% efficient)		
MINE HEATERS			Heat out, exhaust		
Heat in, from			Air compressors	0.04	...
Water (75% of treated water)	36.8	20.0	Water pumps	0.21	...
Steam	29.7	2.48	Generators	0.31	...
Heat out, in			Over-all unit efficiency: $\frac{\text{Lb. water to field} \times (H \text{ at } 326^\circ \text{ F.} - H \text{ at } 77^\circ \text{ F.})}{\text{Heat in}}$		
Process water	66.5	22.48		$\frac{22.5 \times 10^6 \times (296.5 - 45.0)}{7.13 \times 10^6}$	$= 79.3\%$
Losses	Negligible	...			

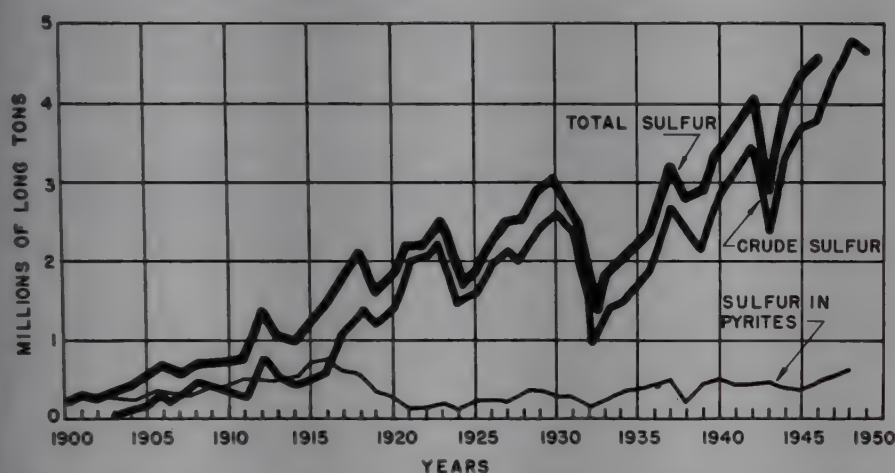


Figure 8. Comparison of Sulfur Production from Mines and from Pyrites

recovering sulfur in a reasonable quantity by that technique. Another source which could prove significant is oil shale, providing commercial exploitation of that material for oil is made.

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PROCESSING EQUIPMENT

- (1E) Filtrol Corp., Los Angeles, Calif., Filtrol clay.
- (2E) Marley Co., Inc., Kansas City, Kan., one-piece spray nozzles.
- (3E) Morris Machine Works, Mechanicsville, N. Y., 4-inch, 470-gal./min. pumps.
- (4E) Permutit Co., New York, N. Y., hot lime-soda water conditioners.

Sulfur from Sour Gases



Specially Designed Combustion Furnace, Left, Used in Mathieson Chemical Corporation's Sulfur Recovery Process

FREDERICK G. SAWYER¹

AND

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VIEWED in the light of present-day demands for both petroleum products and sulfur, and the dwindling of our easily accessible reserves in both categories, the utilization of sour petroleum crudes and sour natural gases takes on increasing importance. The presence of hydrogen sulfide and mercaptans in sour crudes renders these products unfit for most uses because of the toxic nature of the contaminants and the corrosive conditions obtained on oxidation. The presence of hydrogen sulfide in natural and refinery gases has limited the use of these gases to boiler fuel. There are vast quantities of sour natural gas in this country, only small amounts of which are currently being utilized; they are being held in reserve until the short supply of sweet gas is exhausted.

Many satisfactory methods have been developed for the removal of hydrogen sulfide from hydrocarbon gases (10, 11, 21-24, 26). These methods all depend on absorption of the hydrogen sulfide in a weakly alkaline solution, followed by regeneration of the absorbing solution, usually by heating. Commonly used

absorbants include ethanalamines (Girbotol process, 22), tri-potassium phosphate (Shell Development Company, 24), sodium phenolate or sodium carbonate (Koppers Company, 21), and sodium thioarsenate (Koppers Thylox process, 11, 21).

Of the above processes, the Thylox process is unique in that the scrubbing solution is regenerated by air oxidation rather than by heating, the regeneration resulting in the formation in the solution of an elemental sulfur suspension. The sulfur is removed by flotation, and is filtered and dried. Other processes use the oxides of iron or nickel in an alkaline solution, and produce sulfur by oxidation in a similar manner.

In the gas cleaning processes in which solution regeneration is effected by heating to drive off the dissolved acid gases, a gas relatively rich in hydrogen sulfide is obtained as a by-product. The utilization of this gas is doubly important because of the economic value of the sulfur represented and the extremely toxic nature of hydrogen sulfide. In cases where the hydrogen sulfide cannot otherwise be used, it is burned from a flare; the resulting sulfur dioxide is dissipated into the atmosphere. It is much more

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desirable, of course, to recover the sulfur, thus producing a valuable chemical raw material, while minimizing or eliminating entirely any atmospheric contamination.

Except in special cases in which there may be other uses for hydrogen sulfide, it is generally most useful to oxidize the gas to either sulfur or sulfuric acid. Even when sulfuric acid is to be the finished product, there is good reason for making sulfur as an intermediate, for the use of hydrogen sulfide presents several problems. If it is desired to produce sulfuric acid directly from hydrogen sulfide gas, the gas is first burned to sulfur dioxide in an 8 to 10% excess of air. The furnace gas must be cooled to moderate temperature to be thoroughly dried, an expensive process attended by serious corrosion problems. The dry cold gas must then be reheated to converter temperature before it is finally converted to sulfuric acid by the contact process.

In the production of acid from sulfur, a burner exit gas containing 7 to 11% sulfur dioxide is readily produced. If raw hydrogen sulfide is used directly, mixed as it often is with carbon dioxide and a small portion of hydrocarbon gases from the solution regeneration system, a converter inlet gas containing a smaller percentage of sulfur dioxide is formed, and a larger acid plant size is required for the same acid production. Furthermore, so much water forms by oxidation in this method that unless strong acid produced from sulfur is available, concentration of the tower acid is required.

A further advantage of preparing sulfur as an intermediate in the process is the significant alleviation of storage problems. The provision of facilities for large scale sulfuric acid storage is costly and cumbersome in comparison with the simple, outdoor stockpiling of elemental sulfur. Thus in practically every case, elemental sulfur is the most desirable form in which to recover the sulfur from hydrogen sulfide.

HISTORY OF CLAUS-CHANCE PROCESS

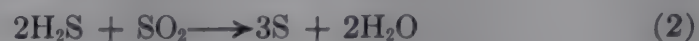
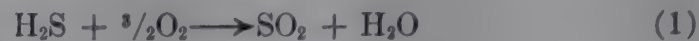
The recovery of sulfur from hydrogen sulfide is a very old process (12, 17, 18). Perhaps the earliest commercial venture was the English Claus (6) (later Claus-Chance, 3) process, involving the direct combustion of hydrogen sulfide gas in air.

The combustion reaction was carried out in a kiln packed with bog-iron ore. The kiln was made very large to provide for dissipation of heat by radiation from its surface, and was fed slowly enough to prevent excessive temperature rise, eliminating the side reaction between sulfur and oxygen to form sulfur dioxide. (Sulfur dioxide formation could be prevented in this manner because the reaction of hydrogen sulfide with oxygen to form sulfur takes place at temperatures lower than those required for the competing reaction between sulfur and oxygen. Maintaining lower temperatures also prevented the reaction between sulfur and carbon dioxide to form sulfur dioxide and carbon monoxide.)

A large part of the product from the Claus kiln was recovered as molten sulfur collected in a receiver just outside the kiln; the sulfur not condensed in the receiver was collected in a dust chamber. Sulfur dioxide was removed from the stack gas by solution in water in a wash tower. Excess hydrogen sulfide was finally removed by passing the gas stream through an iron oxide purifier, or through a fire where the hydrogen sulfide was burned to sulfur dioxide and carried through flues to a chimney (12, 17, 18).

The success of the Claus-Chance process depended on operating the furnace or kiln at a temperature of about 500° F. as measured in the exit pipe. This temperature was controlled in early plants by regulating the inlet hydrogen sulfide gas and air flow, cutting the flow if the temperature became too high. In later modifications, if the furnace temperature began to climb, a portion of the stack gas was recirculated through the kiln to dilute the reacting gases and lower the reaction temperature. The result of excessive furnace temperatures was the reaction of part of the oxygen with sulfur rather than with hydrogen sulfide, lowering the yield.

In modifications developed later by the I. G. Farbenindustrie, A.-G., and by Baehr (1), emphasis was placed on the recovery of sulfur from hydrogen sulfide and sulfur dioxide by contact catalysis. One third of the initial hydrogen sulfide stream was burned to sulfur dioxide; the latter then reacted catalytically with the remaining two thirds of the initial hydrogen sulfide feed stream to yield elemental sulfur.



In this way the process made possible higher yields of sulfur from the hydrogen sulfide, in spite of sulfur dioxide formation in the furnace. All processes in use today for the recovery of sulfur from hydrogen sulfide depend on the reactions involved in the old Claus processes (2).

PILOT PLANT DEVELOPMENT OF MATHIESON PROCESS

With the discovery of extensive sour gas fields in southern Arkansas, investigation was begun to determine the feasibility of sweetening the gas for use in domestic and commercial applications (27). The raw gas contained about 8% hydrogen sulfide and about the same concentration of carbon dioxide. It was found that the gas could be economically sweetened by ethanalamine absorption (22), which separated the hydrogen sulfide from the gas and liberated it in a concentrated side stream. In 1941, the Southern Acid and Sulphur Company, now a part of the Mathieson Chemical Corporation, engaged the Ohio State University Research Foundation to search the literature and develop in the laboratory a process for the recovery of sulfur from the acid gas separated from Arkansas sour natural gas.

As a result of the literature survey, the Claus-Chance reaction was chosen as providing a basis for the most promising method of sulfur recovery. On the basis of laboratory studies, a pilot plant with a capacity of 100 pounds per hour was erected in 1941 near Magnolia, Ark., for further study of the process and the collection of reliable process data for design purposes. This pilot plant was operated jointly by personnel from the Southern Acid & Sulphur Company and the Ohio State University Research Foundation. (About this same time, Susearch, an affiliate of the Texas Gulf Sulphur Company, built its pilot plant at McKamie, Ark., and started an independent study of the utilization of hydrogen sulfide derived from sour natural gases, 16.) Considerable study on furnace design was required in Southern's Magnolia pilot plant, because furnace operation on the larger scale was found to be much more troublesome than laboratory results had indicated. The difference arose chiefly because in the laboratory the furnace had been externally heated with easily controlled electric heaters. This factor, plus the high ratio of area to volume in the laboratory furnace, had made the operation very easy to perform. After much pilot plant investigation, a satisfactory furnace design was evolved, and application of the pilot plant design to a commercial kiln resulted in a smoothly functioning process.

In addition to the vital furnace design data which the pilot plant supplied, it also demonstrated the feasibility of using sulfur cooling towers to separate the sulfur produced. Converter size requirements and heat exchanger duties also were ascertained in the pilot plant stage.

MATHIESON COMMERCIAL PLANTS

On the strength of laboratory and pilot plant data, a commercial plant with a capacity of 120 to 150 long tons per day was designed by the Foster-Wheeler Corporation, New York, in close cooperation with Southern's pilot plant engineers. The plant, based on processes covered by patents and patent applications coming from the developmental work (8, 9, 19, 20), was erected



Acid Gas from Sweetening Plant Enters Mathieson's McKamie Plant through Knockout Drum, Foreground

Air and acid gas are admitted to horizontal kiln where mixing and controlled partial combustion occur

at McKamie, Ark., by the Fluor Corporation, Los Angeles, Calif., and began operation on March 9, 1944.

Early in February 1946, a second plant was brought into operation near Magnolia, Ark. This plant, built by the Foster-Wheeler Corporation, is of a design similar to that of the McKamie plant, the chief difference being in the use of steam-driven equipment at Magnolia instead of the electric motor drives employed at McKamie. Both these plants are now operating to produce a high grade (99.97%) sulfur, which is used ultimately in the manufacture of sulfuric acid.

Process Description. The process flow sheet for Mathieson's sulfur recovery plants in Arkansas is shown in Figure 1, and a complete material balance is given in Table I.

In this process hydrogen sulfide from the monoethanolamine stripper is delivered to the plant at a very low positive pressure (5 pounds per square inch gage), saturated with water vapor at the pressure and temperature of the gas, which is in the range 100° to 150° F. Entrained water vapor is removed from the inlet gas by means of a knockout drum; the gas then passes without further treatment to the combustion furnace (19, 20). Air for the combustion is supplied by a positive displacement rotary blower (5A). The ratio of air to acid gas is manually controlled by means of a by-pass on the air line, in order to provide the

correct amount of air for complete combustion of the hydrocarbons, and oxidation of the hydrogen sulfide to sulfur.

Combustion Furnace. The plant at McKamie, which is the larger of the two Mathieson plants, includes a cylindrical combustion furnace, or horizontal kiln, 9 feet in diameter by 22 feet long. The kiln is divided laterally into three sections, with manifold connections for parallel operation. Each of the three sections is complete in itself (see Figure 2).

The total heat release in the furnace is about 15,000 B.t.u. per hour per cubic foot of furnace volume, an amount much greater than that obtained in the old Claus-Chance furnace. This heat release in partial combustion is made possible by the special design of the furnace, which operates on a recuperative heating principle, each section of the kiln containing its special recuperative heater and special packing section to assure uniform oxidation. The furnace is shown in title photo of this paper; air flow is controlled manually to ensure the proper air-to-acid gas ratio, providing for oxidation of the hydrogen sulfide to sulfur.

The inlet air and acid gas are preheated within the furnace by indirect heat exchange with the products of combustion. Combustion takes place in each section in a region loosely packed with high temperature firebrick. The need for such packing had been demonstrated in the pilot plant studies, where it was found that in the absence of packing the reaction front moved out through the exit end of the furnace, and combustion was eventually extinguished in the line. This difficulty was eliminated through the combined use of recuperative heating and

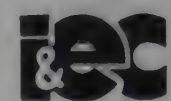
added reaction surface to promote combustion inside the furnace.

Each of the three combustion chambers is provided with a port which will allow insertion of a natural gas burner for preheating the furnace. On a start-up after a prolonged shutdown, the burners are installed and natural gas is burned in the equipment until the minimum operating temperature of 1800° F. is reached. The burners are then removed, the ports are blanked, and the acid gas and air feed streams are started. Preheating the plant by this method requires about 72 hours.

After a plant shutdown of 60 hours or less, the auxiliary gas burners are not required; resumption of operations is attained merely by readmitting the gas streams to the equipment. No provision is made for igniting the acid gas in the furnace.

A waste heat boiler is used to cool furnace exit gases prior to admitting them to the converters. The boiler, along with a feed-water economizer (3A), recovers sufficient heat to generate 5000 pounds of 300 pounds per square inch gage saturated steam for each long ton of sulfur produced. After leaving the boiler, the gases are further cooled in a shell-and-tube gas-to-gas heat exchanger, and then are led to the first converter.

Catalytic Converters. In order to make possible the high volume throughput used in the Mathieson process, as compared to the old Claus-Chance process, and in any case to obtain



PLANT PROCESS SERIES

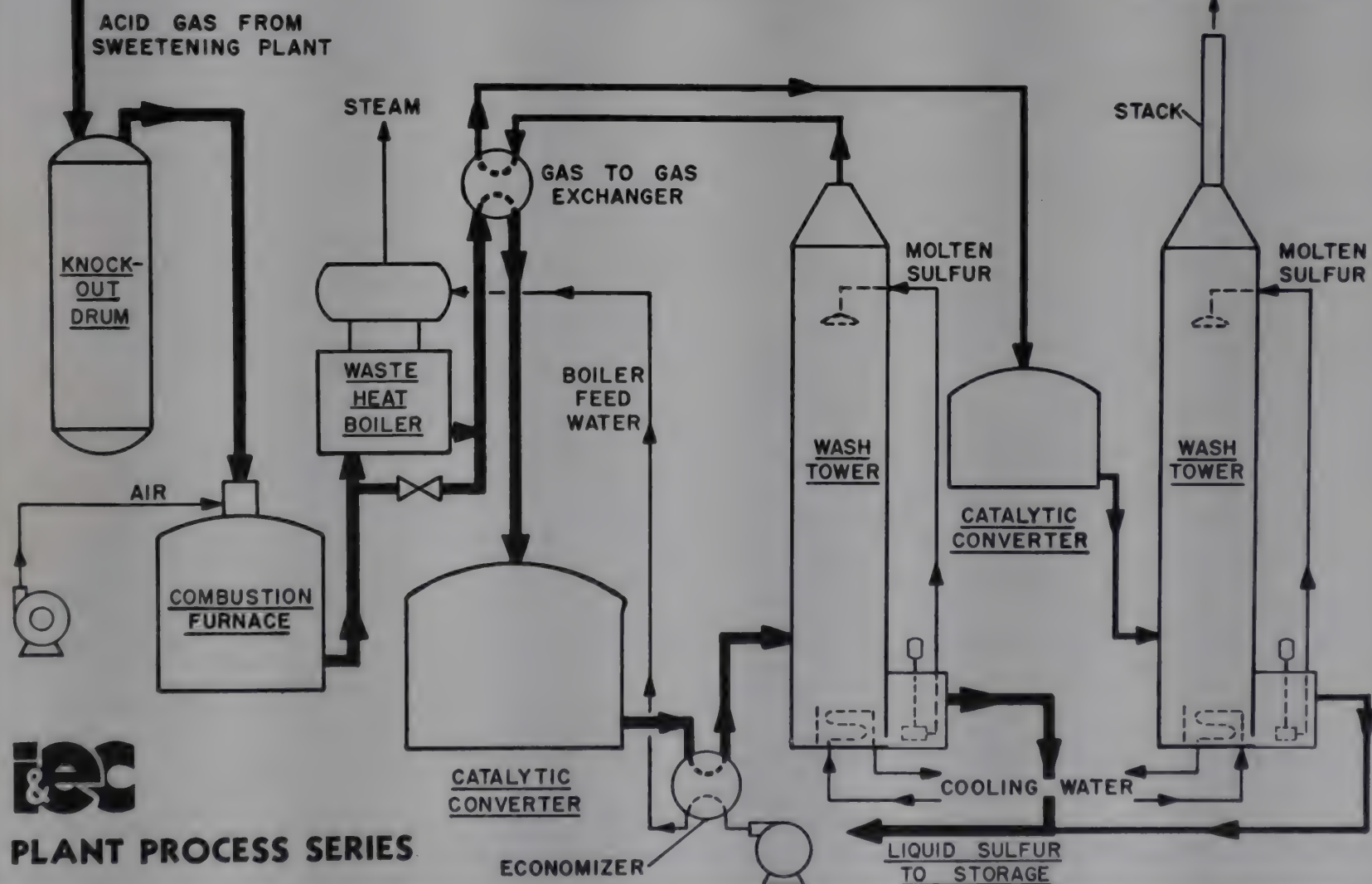


Figure 1. Flow Sheet for Recovery of Elemental Sulfur from Sour Natural Gases by Mathieson Chemical Corporation's Process

TABLE I. MATERIAL BALANCE

Basis. Design for 120 Tons of Sulfur per 24 Hours, Available as Hydrogen Sulfide^a for Plant Feed

ACID GAS ANALYSIS^b (WATER-SATURATED AT 5 LB./SQ. INCH, 120° F.)

	%
H ₂ S	53.92
CO ₂	34.75
CH ₄	2.74
H ₂ O	8.59
	100.00

AIR ANALYSIS^c (50% SATURATED AT 100° F.)

	%
O ₂	20.13
N ₂	76.64
H ₂ O	3.23
	100.00

^a 1,000,000 cu. feet H₂S at 14.7 lb./sq. inch gage, 60° F., contains 38.17 tons sulfur equivalent.

^b Varies with variations in temperature and pressure.

^c CO₂ and rare gases neglected.

MATERIAL BALANCE OF PLANT ENTRANCE GAS BY ELEMENTS, POUNDS PER HOUR (FEED, 52,800 POUNDS PER HOUR)

	H ₂ S	CO ₂	H ₂ O	CH ₄	O ₂	N ₂	Total
H ₂	700	...	177	70	947
S	11,200	11,200
O ₂	...	7,182	1,418	...	6,720	...	15,320
C	...	2,693	...	210	2,903
N ₂	22,430	52,800
	11,900	9,875	1,595	280	6,720	22,430	52,800

$$\frac{11,900 \times 24 \times \frac{32}{34}}{2240} = 120 \text{ long tons per day equivalent}$$

$$120 \times 91.7\% \text{ yield} = 110 \text{ long tons per day rated output}$$

MATERIAL BALANCE, McKAMIE PLANT, AT 110 TONS PER DAY OUTPUT

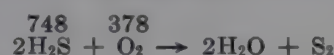
Calculation of Acid Gas Required for 110-Ton-Per-Day Sulfur Production at 91.7% Yield

$$\frac{110 \times 2240}{24 \times 91.7\% \text{ yield}} \times \frac{34}{32} = 11,900 \text{ pounds H}_2\text{S per hour}$$

$$\frac{11,900}{34} \times 374 = 131,000 \text{ cu. feet H}_2\text{S per hour}$$

$$\frac{131,000}{53.92} = 243,000 \text{ cu. feet acid gas per hour}$$

Calculation of Air Required for 110-Ton-per-Day Sulfur Production at 91.7% Yield



$$350 \text{ moles H}_2\text{S} \times \frac{378}{2} =$$

$$\text{Cu. feet O}_2 \text{ required per hour} = 66,200$$



$$17.5 \text{ moles CH}_4 \times 756 =$$

$$\text{Cu. feet O}_2 \text{ required per hour} = 13,240$$

$$\frac{79,440}{20.13} = 395,000 \text{ cu. feet air per hour}$$

MATERIAL ENTERING FURNACE

Gas	Lb./Hr.	M.W.	Moles	Cu. Ft./Hr.	Vol. % of Mixture
H ₂ S	11,900	34	350	131,000	20.52
CO ₂	9,875	44	224.3	84,400	13.23
CH ₄	280	16	17.5	6,600	1.03
H ₂ O	1,595	18	88.6	33,520	5.25
N ₂	22,430	28	801.0	303,000	47.48
O ₂	6,720	32	210.2	79,440	12.49
Total	52,800		1691.6	637,960	100.00

MATERIAL CARRIED BY GASES FROM FURNACE (1900° F.) TO BOILER

Gas	Lb./Hr.	M.W.	Moles	Cu. Hr.	Vol. %
H ₂ S	4,930	34	77.0	29,000	4.70
SO ₂	9,240	64	154.0	58,200	9.43
COS	4,499	60	102.3	38,700	6.27
CO ₂	7,895	44	179.4	66,000	10.66
CH ₄	280	16	17.5	6,600	1.03
H ₂ O	1,595	18	88.6	33,520	5.25
N ₂	22,430	28	801.0	303,000	47.48
O ₂	6,720	32	210.2	79,440	12.49
S ₂ vapor	3,806	64	59.5	22,500	3.64
Total	52,800		1,632.4	617,100	100.00

MATERIAL CARRIED BY GASES FROM BOILER (750° F.) TO NO. 1 CONVERTER

Gas	Lb./Hr.	M.W.	Moles	Cu. Ft./Hr.	Vol. %
H ₂ S	2,618	34	77.0	28,800	4.61
SO ₂	4,930	64	77.0	29,000	4.64
COS	4,620	60	77.0	29,100	4.66
CO ₂	7,250	44	165.3	62,100	9.94
H ₂ O	7,138	18	397.0	150,000	24.02
N ₂	22,430	28	801.0	303,000	48.52
O ₂
S ₂ vapor	3,806	64	59.5	22,500	3.61
Total	52,800		1,653.8	624,500	100.00

MATERIAL CARRIED FROM NO. 1 CONVERTER TO ECONOMIZER

Gas	Lb./Hr.	M.W.	Moles	Cu. Ft./Hr.	Vol. %
H ₂ S	1,113	34	32.8	12,250	2.05
SO ₂	1,046	64	16.3	6,126	1.02
CO ₂	10,632	44	241.8	90,700	15.17
H ₂ O	7,950	18	442.0	167,000	27.90
N ₂	22,430	28	801.0	303,000	50.70
S ₂ vapor	9,629	192	50.1	18,900	3.16
Total	52,800		1,584.0	597,976	100.00

MATERIAL CARRIED FROM ECONOMIZER TO NO. 1 TOWER

Gas	Lb./Hr.	M.W.	Moles	Cu. Ft./Hr.	Vol. %
H ₂ S	1,113	34	32.8	12,250	2.10
SO ₂	1,046	64	16.3	6,126	1.05
CO ₂	10,632	44	241.8	90,700	15.52
H ₂ O	7,950	18	442.0	167,000	28.61
N ₂	22,430	28	801.0	303,000	51.80
S ₂ vapor	3,050	192	15.9	5,390	0.92
S ₂ liquid	6,579	256	25.6
Total	52,800		1,575.4	584,466	100.00

MATERIAL CARRIED FROM NO. 1 TOWER TO NO. 2 CONVERTER

Gas	Lb./Hr.	M.W.	Moles	Cu. Ft./Hr.	Vol. %
H ₂ S	1,113	34	32.8	12,250	2.11
SO ₂	1,046	64	16.3	6,126	1.05
CO ₂	10,632	44	241.8	90,700	15.66
H ₂ O	7,950	18	442.0	167,000	28.84
N ₂	22,430	28	801.0	303,000	52.33
S ₂ vapor	23	192	0.16	45	0.01
Recovered S liquid	3,027
Total	46,221		1,534.06	579,121	100.00

6,579 lb. sulfur condensed in economizer.
52,800

MATERIAL CARRIED FROM NO. 2 CONVERTER TO NO. 2 TOWER

Gas	Lb./Hr.	M.W.	Moles	Cu. Ft./Hr.	Vol. %
H ₂ S	265	34	7.76	2,910	0.50
SO ₂	248	64	3.88	1,460	0.25
CO ₂	10,632	44	241.80	90,700	15.73
H ₂ O	8,399	18	467.00	176,000	30.54
N ₂	22,430	28	801.00	303,000	52.57
S ₂ vapor	1,220	192	6.36	2,400	0.41
Total	43,194		1,527.80	576,470	100.00

6,579 sulfur condensed in economizer
3,027 sulfur condensed in No. 1 tower
52,800

EXIT FROM NO. 2 TOWER THROUGH STACK

Gas	Lb./Hr.	M.W.	Moles	Cu. Ft./Hr.	Vol. %
H ₂ S	265	34	7.76	2,910	0.50
SO ₂	248	64	3.88	1,460	0.25
CO ₂	10,632	44	241.80	90,700	15.80
H ₂ O	8,399	18	467.00	176,000	30.66
N ₂	22,430	28	801.00	303,000	52.78
S ₂ vapor	23	192	0.16	45	0.01
Total	41,997		1,521.60	574,115	100.00

6,579 sulfur condensed in economizer
3,027 sulfur condensed in No. 1 tower
1,197 sulfur condensed in No. 2 tower
52,800



Converters and Wash Towers

Furnace exit gases are treated in first converter (on concrete platform); elemental sulfur is condensed in first tower (center), and gases are passed to second converter; final tower completes removal of elemental sulfur from gases, which are discharged through stack into atmosphere. Molten sulfur is collected in subterranean pit, foreground, and periodically pumped to tank cars for shipment

a recovery of over 80%, it was found necessary to include catalytic converters for further treatment of the furnace exit gases. In the plant at McKamie, for example, two converters in series are used. These are of a mushroom type, in separate shells, with the gases passing downward through the catalyst beds (see Figure 3). Gas enters each converter in the center of the dome, is deflected radially by means of a single flat mild steel deflector, and then descends through the catalyst (6- to 8-mesh Porocel, a high-iron activated bauxite) which is supported on a stainless steel screen resting on a cast iron grate. The first converter stage at McKamie is operated with a catalyst bed temperature of about 750° F., with the second stage at about 500° F.

The catalyst beds are covered with a thin layer of firebrick to minimize any tendency of the catalyst toward agitation in the gas stream. Two exit ports, spaced 180° apart, were provided in the shell of McKamie's first converter, and one such port in the second smaller converter. With this arrangement there has been no evidence of gas channeling, and no temperature disproportionation over the cross section of either catalyst bed. An auxiliary burner port similar to those in the furnace has been provided in each converter. Natural gas burners are used here also in a start-up, to bring the converters up to a minimum temperature of 500° F. before starting production.

Bauxite-type catalysts have proved to be of most general utility in the recovery of sulfur. They are mechanically strong, economical to install, and long-lasting in activity (7-15). To date, no limit on the life of the catalyst has been observed. In plant use, however, the catalyst particles may become coated with carbon deposits, causing increased pressure drop through the bed. To avoid excessive pressures, therefore, the catalyst is changed every 3 to 5 years.

In contrast to the furnace, or kiln, in which operating variables can be varied only within a very narrow range, converter operation can be greatly varied to obtain the best operating conditions. The principal independent variables are: bed temperature, bed depth, and gas velocity (bed transverse area). A fourth important variable, but one over which control is not easily maintained, is the water content of the gas stream. Other gas component concentrations are of considerably less importance.

All elemental sulfur formed in the kiln is allowed to remain in the gas stream to the first converter, as it does not affect the reactions occurring there. In order to obtain the highest possible conversion in the second stage, the sulfur produced in the kiln and the first converter is removed prior to admission of the gas to the second converter stage. This lowers the sulfur dew point of the second converter exit gas.

Sulfur Wash Towers. The gas from the first converter is cooled by passage through the boiler feedwater economizer (3A) and then admitted to the first sulfur tower. A grid-packed cooling tower is used for sulfur removal at this point (see Figure 4). In the sulfur tower, the gases from the first converter are further cooled by passage up through the tower, countercurrent to a stream of molten sulfur. The heat absorbed from the hot gases and from the condensation of the sulfur vapor is removed by indirect heat exchange between the sulfur and cooling water in the sulfur sump located beneath the tower. By maintaining the sulfur at a temperature just above the melting point and by the use of an efficient mist separator in the final tower, a stack gas containing less than 0.1% sulfur vapor can be realized.

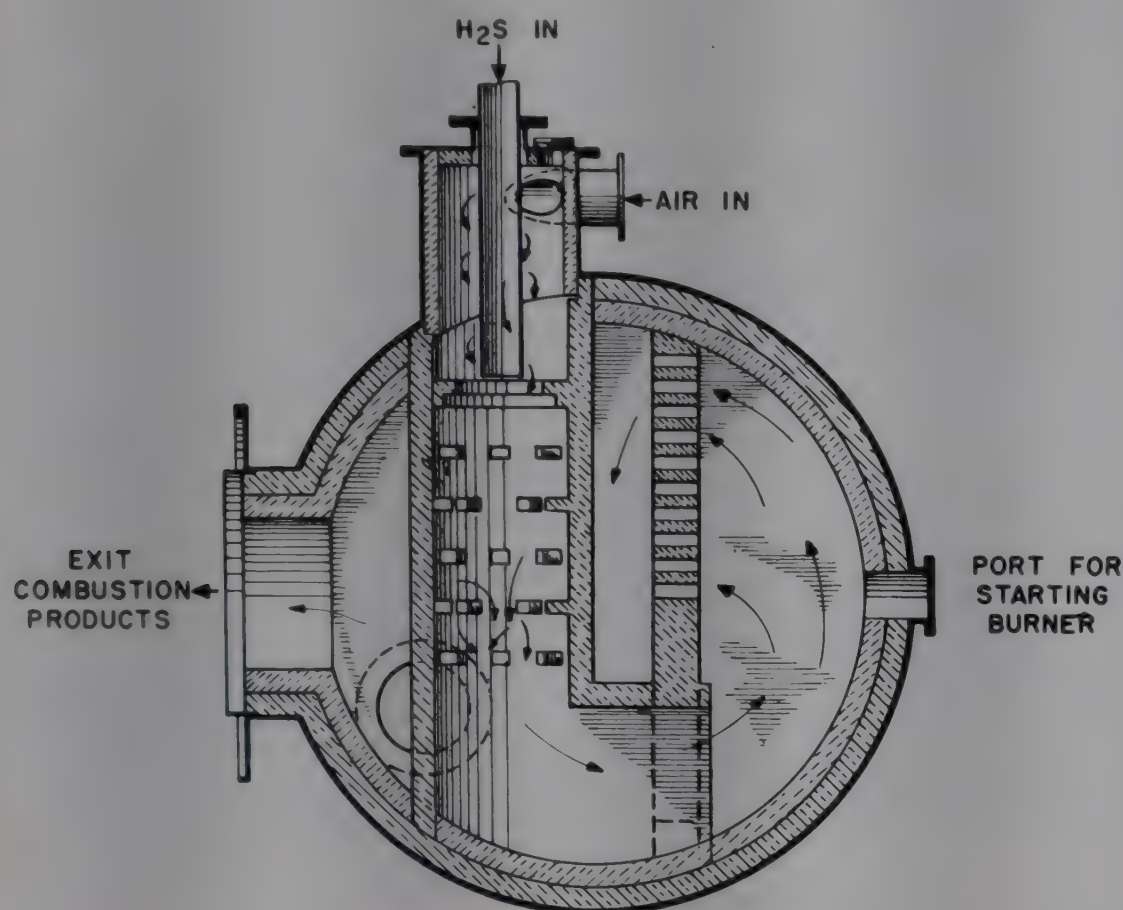


Figure 2. Combustion Furnace

The gas leaving the first tower at a temperature of 270° F. is reheated in the gas-to-gas heat exchanger to 450° F. The reheated gas is passed to the second converter, and thence to the final tower, which is the last piece of major processing equipment in the recovery process.

The sulfur towers used at McKamie are constructed of unlined mild sheet steel, and are "packed" with angle irons welded in place in staggered horizontal rows. For ease of construction the towers were made square in cross section (8 × 8 feet). Liquid sulfur is pumped over the tower packing at a temperature of 250° to 275° F. by submerged centrifugal cast iron pumps (4A). The product sulfur flows from the towers to a rundown pit, from which it is pumped periodically to tank cars for shipment.

MATERIALS OF CONSTRUCTION

All plant equipment which is to be subjected to high internal temperatures is constructed of mild steel insulated with fire clay, except for the heat transfer surfaces, which are of corrosion-resistant Type 430 stainless steel (1A). The refractory-lined portion of the plant includes the furnace, boiler, first converter, and intermediate duct work. There are no unusual or elaborate features in any of the equipment except for the internal construction of the furnace. Through ceramic protection of the metal surfaces in high temperature areas of the processing equipment, corrosion losses have been held to a negligible figure. With the

exception of a boiler-tube bundle destroyed through the use of untreated water in the early days of operation, no major equipment replacements have been required at McKamie in more than 6 years of production.

PROCESS CONTROL

Control over the plant process is maintained by analyzing the final converter exit gas, and adjusting air flow to provide the desired exit gas composition.

The sample for analysis is taken into a Tutwiler buret by displacement of an aqueous starch solution; the sample is then adjusted in volume to 100 ml., and titrated in the buret with an iodine solution.



This initial titration reveals the total concentration of sulfur dioxide and hydrogen sulfide together in the exit gas. The resulting solution is drawn from the buret, and the blue end-point color is discharged by means of sodium thiosulfate. Sodium hydroxide solution is then used to titrate the liberated acids to the methyl orange end point. If the original iodine solution and the sodium hydroxide solution are of the same normality, then the ratio of alkali to iodine required is 1 when the gas contains only hydrogen sulfide; 2 when the gas contains only sulfur dioxide; and 1½ when hydrogen sulfide and sulfur dioxide are present in the ratio 2 to 1. This alkali-iodine ratio is the basis for plant control via air input, and operators maintain the hydrogen sulfide-sulfur dioxide ratio in the exit stream as near as possible to 2 to 1.

No continuous analyzer has yet been used to indicate or control the condition of the stack gas. Presumably a continuous analyzer could be installed to make the plant operation automatic, but entirely satisfactory operation is obtained through analysis of the gas by plant operators. Completion of the analysis itself requires only about 3 minutes, and because the flow of acid gas to the plant is very uniform, an hourly titration provides adequate control.

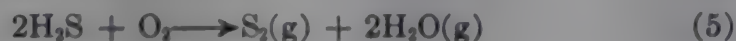
Because so little attention from operators is required, it is estimated that a plant of this type in a size as small as 5 tons of sulfur daily might be operated profitably—especially in a refinery, for example, where operators might be available from other processes.

TABLE II. INSTALLED HORSEPOWER AT MCKAMIE

Equipment	Duty	Hp.
Electrical, 440-Volt, 3-Phase, 60-Cycle		
1 rotary blower (5A)	Air supply to furnace	150
2 sulfur pumps (1 per tower) (4A)	Circulation of liquid sulfur to towers	20 each
1 sulfur product pump (4A)	Removal of finished product to tank cars	20
2 water supply pumps (2A)	Circulation of cooling water to towers	5 each
Lighting		12.5 kv.-amp.
Steam Driven		
2 10 × 6 × 12 Duplex pumps (2A)	Boiler feedwater supply	1 each
2 Coppus TF-9 turbines	Make-up water supply	9 each
1 Coppus TF-9 turbine	Water cooling tower fan	9
2 Coppus TF-12 turbines	Circulating water	12 each

THERMODYNAMICS AND PROCESS VARIABLES

In the old Claus-Chance process, the principal product of furnace reaction was elemental sulfur. This was produced by partial oxidation of the hydrogen sulfide with the theoretical quantity of air, the temperature being maintained at a low level by balancing the heat release against radiation losses. From a thermodynamic standpoint (13, 14), it is found possible to obtain virtually quantitative yields in this manner. For example, for the reaction:



$$\Delta F^\circ = -76,010 - 9.96 T \log T + 5.365 \times 10^{-3} T^2 +$$

$$0.74 \times 10^{-6} T^3 + 32.86 T \quad (6)$$

At 1000° C., the following values are calculated:

$$\Delta F^\circ = -66,340 \text{ cal.}$$

$$K_p = 2.41 \times 10^{11} = \frac{P_{\text{S}_2}(P_{\text{H}_2\text{O}})^2}{P_{\text{O}_2}(P_{\text{H}_2\text{S}})^2}$$

Thus the equilibrium lies far to the right, and substantially complete reaction is thermodynamically possible. Calculations involving the interaction of these gases with other possible products, including sulfur dioxide and carbonyl sulfide, have been made. The results, however, are not appreciably different from those in the simple case as given.

In sharp contrast to the Claus-Chance process, in which sulfur was the principal reaction product, the furnace gas in the Mathieson process is very complex. By way of illustration, data given in Table III show typical analyses obtained in laboratory and plant furnace studies.

A number of observations may be made on the basis of the data in Table III. This particular sample analysis is considered fairly representative of plant operation today, and was chosen for Table III because it included values for all the minor components of the gas.

Furnace Reactions. The principal reactions occurring in the Mathieson process furnace may be written thus:

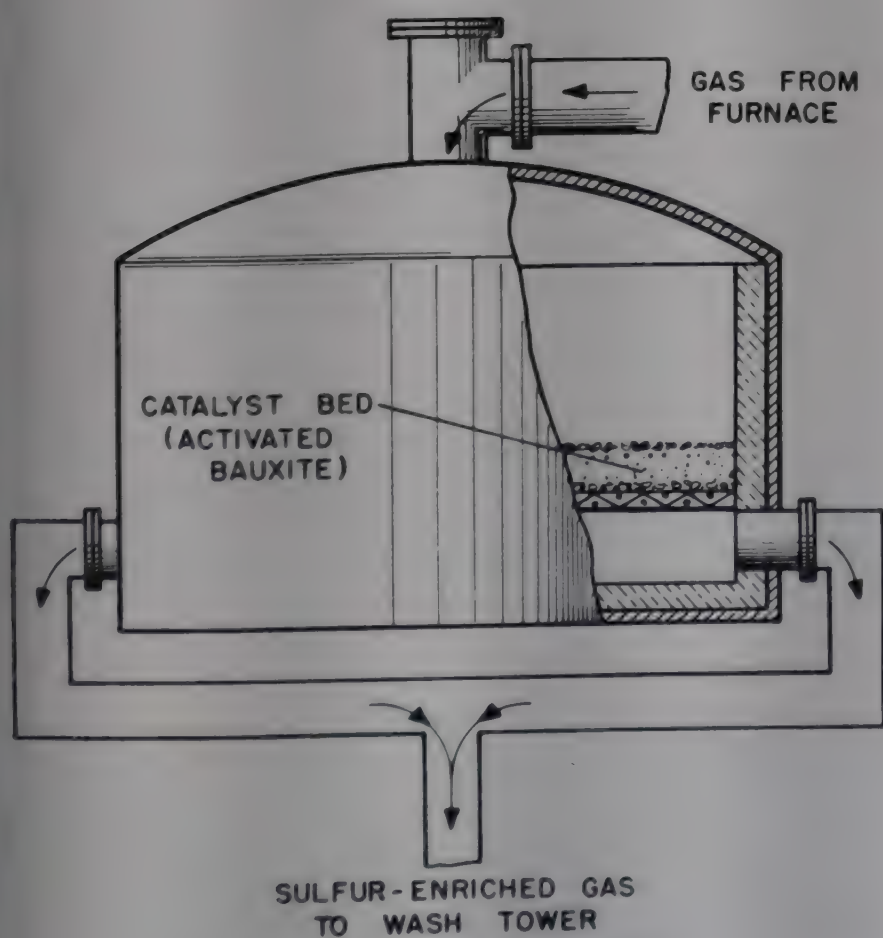
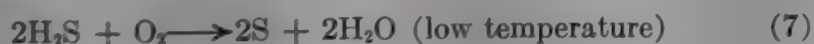


Figure 3. Sulfur Wash Tower

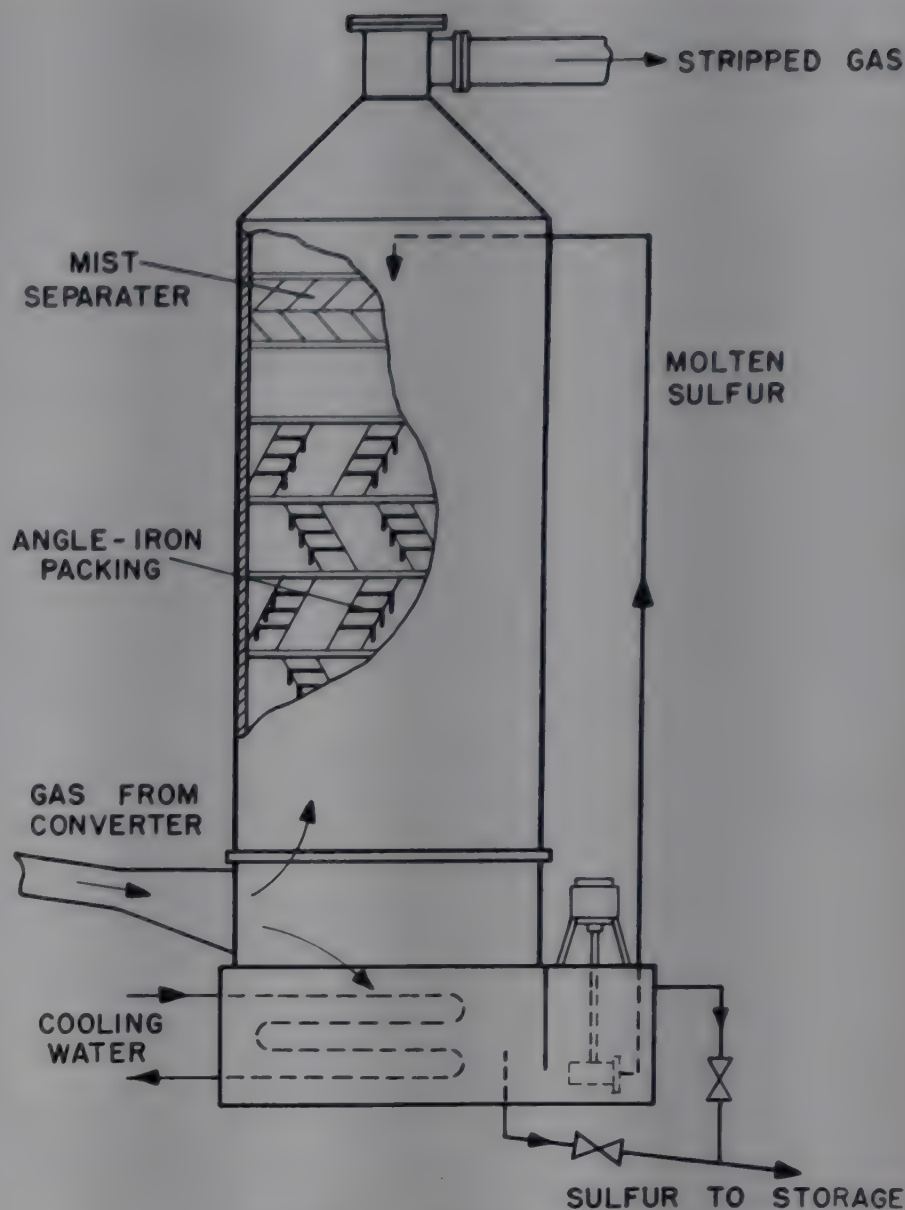


Figure 4. Catalytic Converter



For convenience in heat balance calculations the intermediate mechanisms are not important, and the formation of carbonyl sulfide is represented as shown. It is at once apparent from the data in Table III, however, that the reactions occurring in the furnace are very complex. Hence, furnace reactions in most cases are not written, but are expressed instead in terms of inlet and exit compositions or flow rates. The presence of carbonyl sulfide in the furnace exit is a recognized fact, but its formation is not clearly understood. At 1000° C., and in the presence of water vapor formed by combustion, equilibrium for Reaction 9 lies far to the left. The formation of carbonyl sulfide under conditions obtaining in the furnace would therefore not be expected.

It is believed that the formation of carbonyl sulfide might be caused by the reaction of nascent sulfur vapor with either carbon monoxide or carbon dioxide. This hypothesis has not been substantiated experimentally, but it has been clearly established that during furnace operation carbon dioxide disappears at a rate greater than that which might be explained by its reduction by hydrogen sulfide to form carbon monoxide, free sulfur, and water. In addition, only small amounts of carbon monoxide have been detected in the furnace exit gases, indicating that Reaction 10 does not occur in the furnace to a great extent.



In cases where appreciable quantities of hydrocarbons were present in the inlet gas, the yield of carbonyl sulfide in the furnace was much greater. This is a further indication that carbonyl sulfide is formed by combination of molecular fragments or intermediate oxidation products, rather than by metathesis, for in-

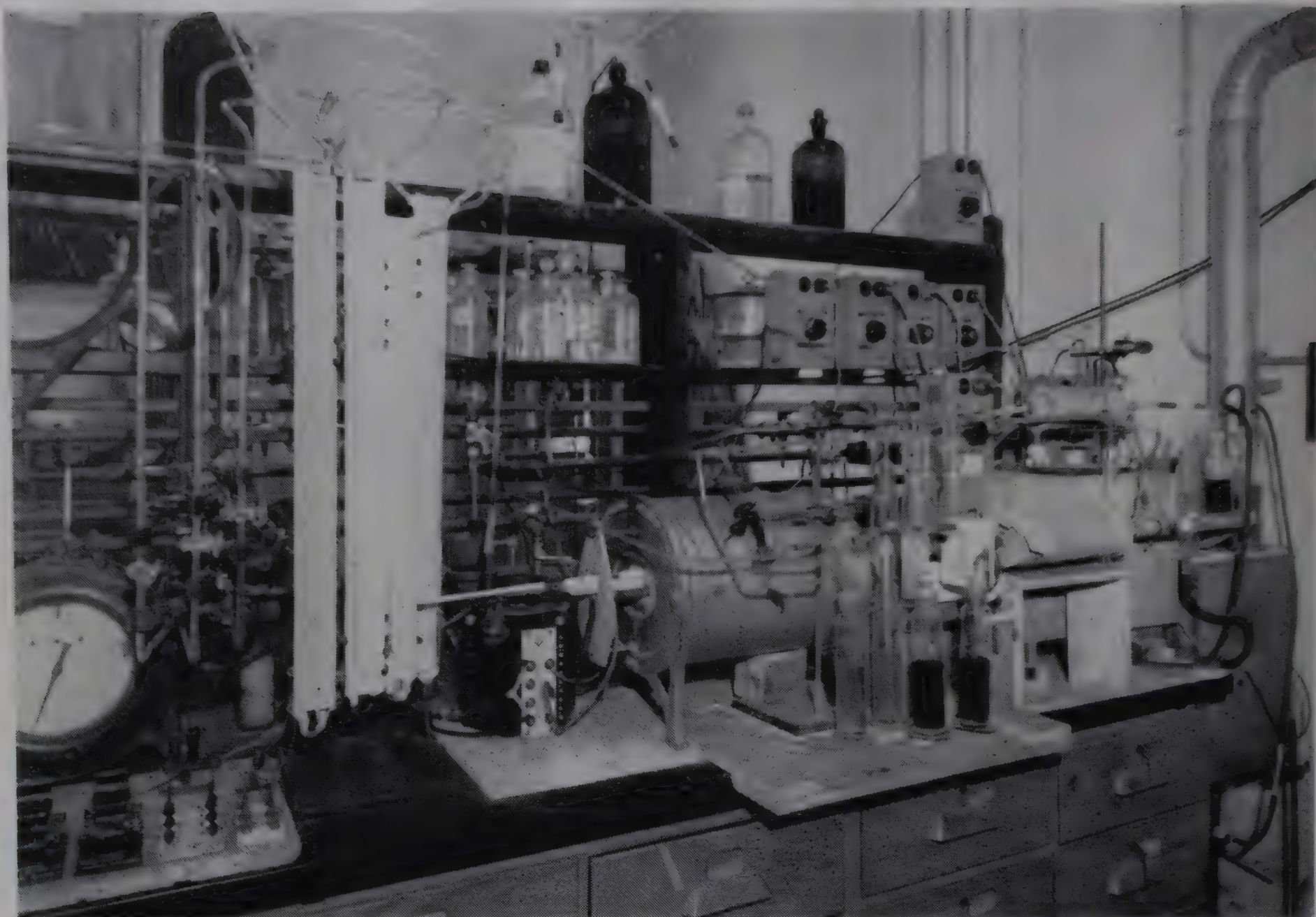


Figure 5. Laboratory Apparatus Used in Evaluating Effects of Process Variables

Included are flowmeters, an electrically heated furnace, boiler, converter (on rack at right), and analytical equipment

stance, between hydrogen sulfide and carbon dioxide. Because the presence of carbonyl sulfide reduces the over-all yield of sulfur in the process, the plant is operated to keep carbonyl sulfide formation at a minimum. Plant studies also revealed that conversions at high temperature were detrimentally affected by the presence of carbon dioxide in the feed stream—probably because of its contribution to carbonyl sulfide formation.

Laboratory Furnace Studies. By far the greatest amount of study of the variables in the Mathieson sulfur recovery process was made on a laboratory scale. Because the laboratory re-

actions paralleled the pilot plant and later the full scale plant reactions, the laboratory observations are worthy of description in some detail.

The laboratory furnace used in early studies was patterned after the Claus-Chance kiln and consisted of a quartz tube, 1 inch in diameter and 18 inches long. In initial experiments, 60 ml. per minute of hydrogen sulfide and 290 ml. per minute of air were passed through this tube at a temperature of 600° to 750° C. In this range, a 76 to 82 mole % conversion of the hydrogen sulfide to elemental sulfur was obtained. The remaining 18 to 24% of the inlet hydrogen sulfide passed through the combustion zone substantially unchanged.

These results were obtained with no packing in the quartz tube; only very slight differences were noted when the tube was packed with iron or cobalt oxides deposited on clay or Carborundum carriers. Varying the temperature up to 900° C. caused no significant deviation from the results obtained at 600° to 750° C.

In later studies, a gas mixture representative of the acid gases produced on sweetening natural gas by ethanolamine absorption was substituted for the hydrogen sulfide. The mixture used was:

H ₂ S	58%
CO ₂	38%
CH ₄	4%

Because hydrogen sulfide is usually removed from natural gas by passing the gas stream through an organic base, it is clear that any carbon dioxide present in the natural gas will be removed concomitantly. (Two major organizations in the field, however, now claim processes which will preferentially separate hydrogen sulfide from sour gases, leaving the carbon dioxide behind, 10, 23.) The ratio of hydrogen sulfide to carbon dioxide removed in any

TABLE III. TYPICAL COMPOSITIONS OF FURNACE GAS STREAMS, MATHIESON SULFUR RECOVERY PROCESS

(Temperature, 1000° C.)

Input gas	Laboratory, Vol. %		McKamie Plant, Vol. %
H ₂ S	63.1	56.6	54.1
CO ₂	36.9	38.8	37.9
CH ₄	0	4.6	1.3
H ₂ O	0	0	6.6
N ₂	0	0	0.1
Furnace exit gas			
H ₂ S	6.4	4.4	0
SO ₂	3.6	3.1	6.42
COS (carbonyl sulfide)	0.9	3.7	5.82
CS ₂	0.24
CO ₂	14.1	13.0	8.01
H ₂ O	19.4	17.7	24.26
CH ₄	0.37
CO	0.1	0.5	0.14
H ₂	..	0.2	0.58
N ₂	0.14
Ar	48.1	51.9	50.29
	7.5	5.5	3.73

process depends on the quantities originally present in the natural gas, on the absorbent used in the operation, and on the completeness of removal of both gases. A small quantity of natural gas is unavoidably dissolved in the absorbent along with the hydrogen sulfide and carbon dioxide, and is liberated on subsequent heating. The quantity of natural gas dissolved depends principally on the operation of the sweetening plant, and is generally in the range of 1 to 4%.

The gas mixture which might be received from a sweetening plant was the subject of extensive study, concentrated on both combustion and subsequent treatment of the furnace exit gas. Special laboratory equipment, suitable for working temperatures of more than 1000° C., was employed in this study, and a porcelain tube served as the furnace, or kiln. The effects of furnace temperature, furnace packing, and space velocity were investigated, using the apparatus as illustrated in Figure 5.

In studying the furnace temperature range likely to be encountered in large scale sulfur recovery from sour refinery gases, the observations collected in Table IV were made using a rich (96%) hydrogen sulfide gas—the type of gas commonly removed from refinery gases by ethanolamine absorption. Conversions were found to decrease slightly with increasing temperature.

TABLE IV. EFFECT OF FURNACE TEMPERATURE ON CONVERSION OF HYDROGEN SULFIDE TO SULFUR

Temperature, ° F.	Conversion %
932	73.1
1065	71.7
1200	70.6

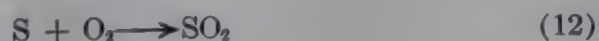
Closely allied with the temperature effect in the furnace is the effect of space velocity on the reaction. The results observed in this investigation are given in Table V, with conversion figures labeled as "apparent." The figures in this column are called apparent because they may not accurately represent the extent of conversion within the furnace proper; there was evidence of continuing reaction in the sampling lines, which had to be maintained at a temperature high enough to prevent the condensation of sulfur vapor. Because the continuing reaction would probably occur with all samples removed under the conditions of this series of tests, however, the trend indicated by the data in Table V is undoubtedly real, with recorded figures being in all cases slightly higher than the true values.

TABLE V. EFFECT OF FLOW RATE ON CONVERSION OF HYDROGEN SULFIDE TO SULFUR

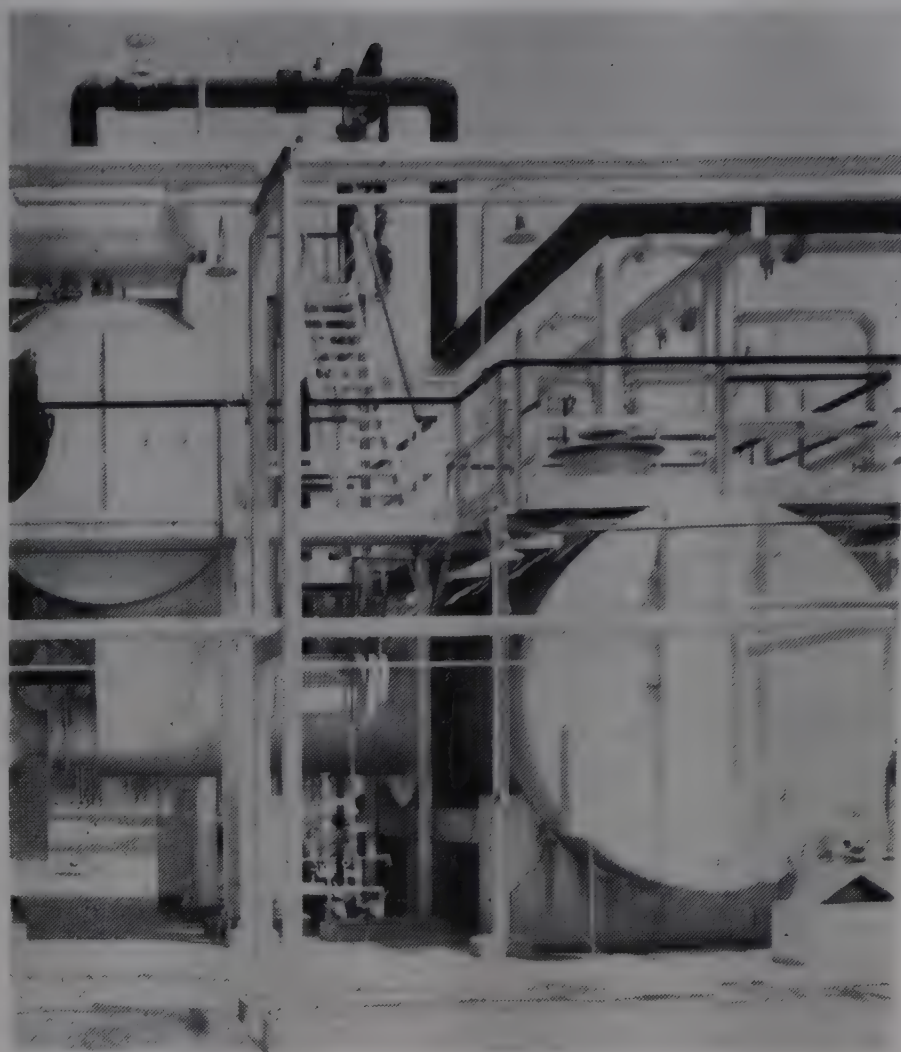
Space Velocity ^a	Apparent Conversion, %
2046	61.8
1764	49
1524	45.3
1014	62.0

^a Volumes of gas (S.T.P.) per unit volume of furnace per hour.

It is well established that the oxidation of hydrogen sulfide is stepwise. Two of the important reactions may be represented as:



It appears that Reaction 11 occurs at a lower temperature than does Reaction 12. As soon as Reaction 11 has begun and sulfur appears in the reaction zone, there is a competition between the sulfur and the hydrogen sulfide for the oxygen present. At lower temperatures, Reaction 12 is suppressed; hence the high conversions to free sulfur at lower temperatures. However,



Horizontal Kiln

Partial combustion occurs in three chambers of kiln, right, and hot exit gases pass through waste heat boiler before entering first converter

as the temperature is increased, Reaction 12 becomes more significant, and a higher percentage of oxygen is consumed in the formation of sulfur dioxide, decreasing the net conversion to elemental sulfur. Thus in the Claus-Chance process a respectable yield of sulfur was obtained by maintaining furnace temperatures at sufficiently low levels.

Confirming evidence was observed in Southern's laboratory work. In the investigation as reported in Table V, there was a space velocity at which the conversion to sulfur reached a minimum. It is believed that at this space velocity, free oxygen existed throughout the furnace length, disappearing only at the exit. At space velocities higher than the critical conditions mentioned, free oxygen would be present in the exit gas. This would react with additional hydrogen sulfide in the comparatively cool sampling lines by Reaction 11, increasing the apparent yield. At space velocities lower than the critical, both Reactions 11 and 12 would occur in the furnace until the oxygen was consumed, after which the sulfur dioxide could react with either the hydrogen sulfide or carbonyl sulfide, increasing the actual furnace conversion.

The effect of additional furnace packing was studied using a 76% hydrogen sulfide gas. Tabular alumina, a porous alumina product of the Aluminum Ore Company of America, was used as packing. The best comparison of results for packed and unpacked reactors, made at space velocities corrected for the presence of the packing, is as follows:

Packing	Space Velocity	Conversion, %
None	1674	71
Tube packed with Al ₂ O ₃	1890	73.3

Allowing for experimental error, it appeared, therefore, that packing was of no significant value in the laboratory furnace. But in the pilot plant it was found that by absorbing heat from the combustion reaction and creating a zone of high temperature,

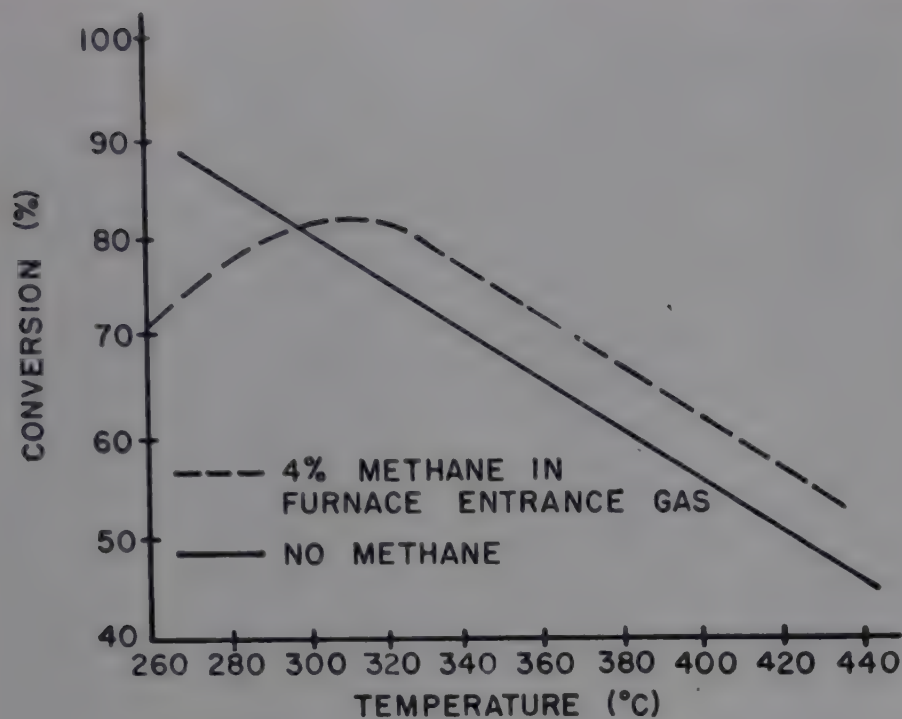


Figure 6. Catalyst Temperature

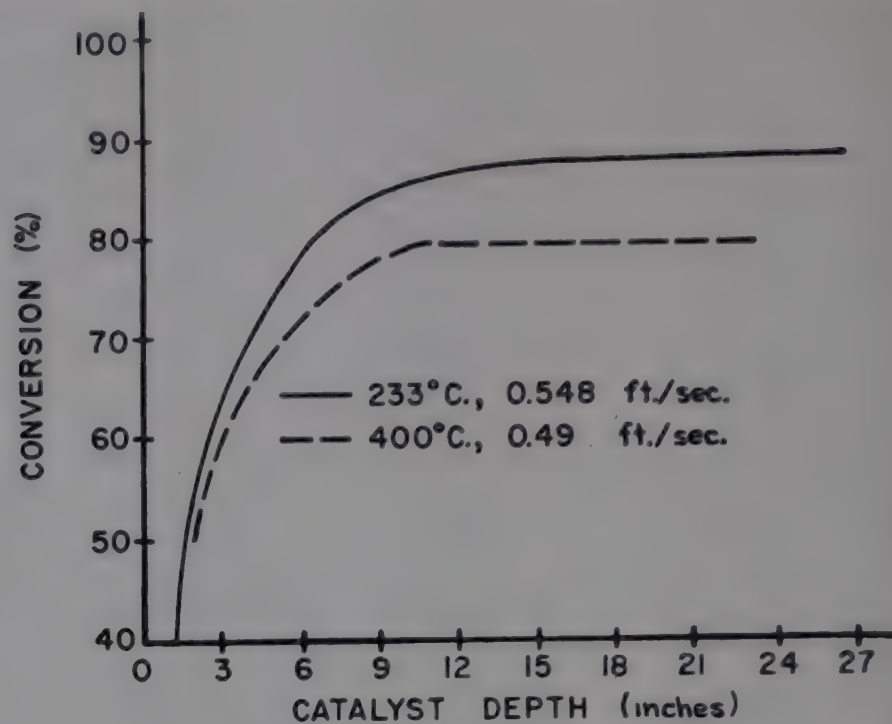


Figure 7. Catalyst Bed Depth

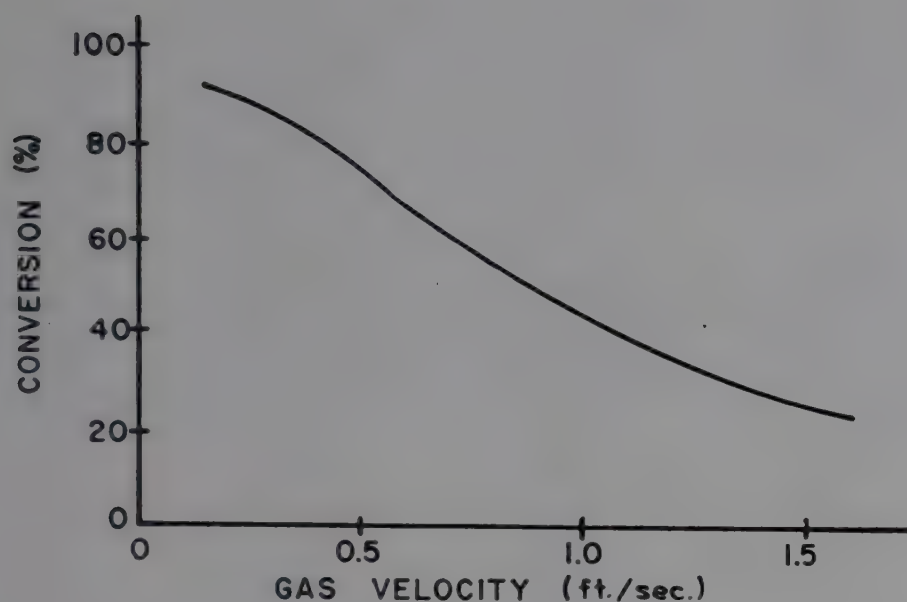


Figure 8. Linear Gas Velocity

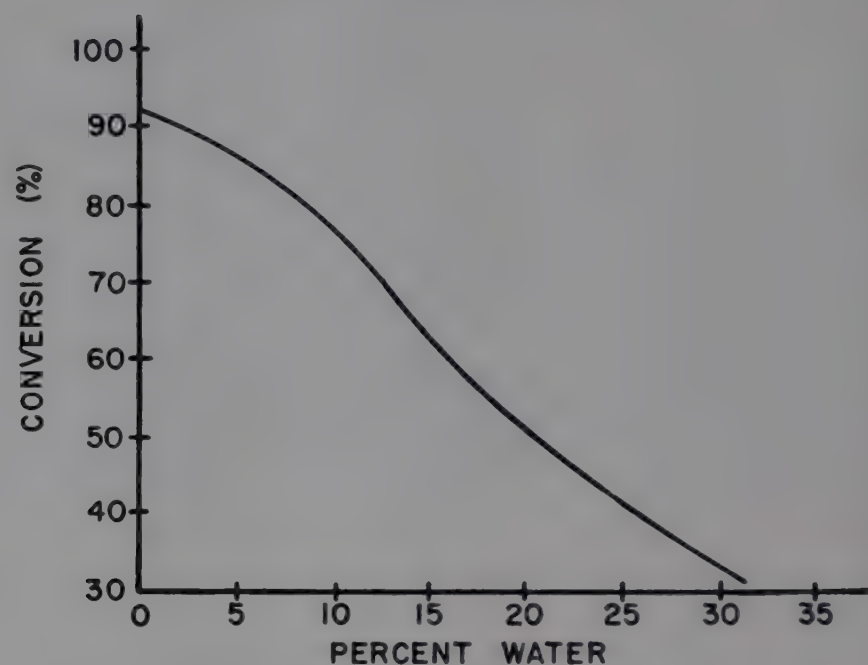
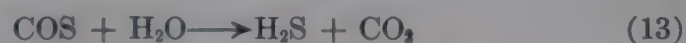


Figure 9. Water Vapor Concentration

Effects of Principal Variables on Conversion as Determined in Laboratory Equipment

packing helped to localize combustion in the proper region, and held the reaction front inside the furnace; the use of firebrick packing in the commercial plant combustion chambers is a result of these findings.

Laboratory Converter Studies. In Mathieson's McKamie plant, the two converter stages are maintained at different temperature levels. In most cases, at least two converters operating under different conditions are deemed essential, because the two reactions required to obtain a high yield of sulfur from the furnace exit gas occur at different temperatures. One reaction involves carbonyl sulfide, and for convenience is spoken of as a hydrolysis; it is the principal reaction in the first converter, which is maintained at about 750° F., and it goes essentially to completion. The mechanism of the reaction is speculative, but the results are known, and suggest the following:



(This reaction is the basis of the method of analysis for carbonyl sulfide in the furnace gas.) The second reaction is:



This reaction occurs to some extent in the first converter, but is incomplete at the high temperature existing there. In the second converter, the gas from the first stage, after removal of the elemental sulfur, is passed through the catalyst at 450°

to 500° F. At this temperature, Reaction 2 goes virtually to completion, and the total recovery of sulfur from the acid gas entering the plant is brought up to 92 to 97%. Both these reactions take place in the presence of the proper catalyst, and so are conveniently used to determine catalytic activity. It is probable that, to a limited extent, other reactions—e.g., between carbonyl sulfide and sulfur dioxide—also occur within the converters.

The effects of the principal variables as determined in laboratory equipment are shown diagrammatically in Figures 6 to 9. In Figure 6, the conversion is shown as a function of catalyst temperature. This particular study represents the conversion of the furnace exit gas components to elemental sulfur. The solid curve represents the case in which the principal reaction involved is that between hydrogen sulfide and sulfur dioxide. Over the entire range studied, the conversion was favored by decreasing temperatures. The second curve in Figure 6 is shown as passing through a maximum conversion at about 320° C. The inlet gas used in this case was obtained by combustion of an acid gas containing 4% natural gas. As shown in the columns under "Laboratory" in Table III, this combustion leads to the formation of large percentages of carbonyl sulfide. At low converter temperatures the carbonyl sulfide passes unchanged through the converter, so that the over-all conversion is found to be low, even though the hydrogen sulfide-sulfur dioxide

reaction is substantially complete. As the temperature is increased, more and more carbonyl sulfide is converted to sulfur, so that the per cent conversion increases. Above 320° C., however, the efficiency of the hydrogen sulfide-sulfur dioxide reaction drops off to such an extent that the over-all conversion to sulfur decreases.

The effect of catalyst bed depth on conversion is shown in Figure 7. The shape of the conversion-catalyst depth curves depends to a large extent on the gas velocity used, but an optimum catalyst depth generally exists for each set of conditions, above which the addition of catalyst has a negligible effect on the conversion obtained. Thus in both the curves shown in Figure 7, a 9-inch bed depth would be considered optimum. At practical space velocities, the optimum bed depth seldom exceeds 22 inches.

Closely associated with the determination of optimum depth of catalyst bed is the study of linear gas velocity through the converter (Figure 8). It is apparent that for a linear gas velocity of 0, equilibrium conditions would be obtained, and that for high gas velocities the conversion would approach 0. The useful range of velocities is included in Figure 8 for the case of a 4-inch catalyst bed. In this range, the conversion decreases in a linear manner with increasing gas velocity, and from the standpoint of seeking high yields, low gas velocities are to be desired. However, converter size requirements increase rapidly at low velocities, so that the range generally used is 0.5 to 2.0 feet per second (S.T.P.).

TABLE VI. SULFUR RECOVERY IN UNITED STATES

Company	Mathieson Chemical Corp. (2 plants)	Texas Gulf Sulfur Co., Inc.	Stanolind Oil and Gas Co.
Location of plants	McKamie, Ark., Magnolia, Ark.	Worland, Wyo.	Elk Basin, Wyo.
Month and year when actual production was begun	March 1944 (McKamie) Feb. 1946 (Magnolia)	April 1950	July 1949
Design capacity, long tons/day	110 (McKamie) 60 (Magnolia)	300	80
Rate of production in actual operation, long tons/day	120 (total)	300	40
Total production in first 6 months of 1950, long tons	25,000	20,000	Not available
Estimated total production in 1950, long tons	50,000	80,000	Not available
Source of gas (or other) feed to recovery plant	Sweetened natural gas	Pure Oil Co.'s River Dome Field near Worland, Wyo.	Natural gas sweetening plant
Composition of gas (or other) feed to recovery plant, %	H ₂ S, 53.92 CO ₂ , 34.75 Hydrocarbons, 2.74 H ₂ O, 8.59	(Before sweetening) H ₂ S, 30 CO ₂ , 2 Hydrocarbons and moisture, 68	H ₂ S, 69.66 CO ₂ , 22.45 H ₂ O, 7.89
Process employed in conversion to elemental sulfur	Modified Claus-Chance	Modified Claus	Modified Claus
Recovery of sulfur in feed stream, %	92-97	90	94
Purity of sulfur produced, %	99.97	99.5	Greater than 99.5
End use of sulfur recovered	Sulfuric acid manufacture	Probably sulfuric acid manufacture	Sold as commercial sulfur

In any catalytic reaction, the presence in the inlet gas of one or the other of the products of reaction may be expected to decrease both the rate of reaction and the equilibrium conversion. That water vapor does decrease the conversion obtainable on a bauxite-type catalyst is shown in Figure 9. The lower the water vapor concentration in the gas, the higher the conversion that may be obtained. Because the water vapor is formed by com-

bustion of hydrogen sulfide and hydrocarbons, this is not a truly independent variable, but depends primarily on the composition of the inlet acid gas. In a given plant a slight increase in conversion will result from lowering the hydrocarbon content in the acid gas being treated. Sizable increases in the hydrocarbon content of the inlet gas require greatly increased air flow for complete combustion, and demand more heat transfer surface for removal of the heat generated. In operation of a plant designed for low hydrocarbon gases, if the hydrocarbon content becomes too high, the total flow of acid gas to the furnace must be cut back to handle the heat transfer, and production is lowered.

PRODUCT PURITY

In contrast with the ordinary sulfur of commerce, the sulfur recovered from natural gas is extremely pure. A sample placed in a casserole and ignited will burn down to a very minute white ash. Even the highest grades of mine-run sulfur can be burned in this manner only if the samples are continually agitated, for they tend to crust over with carbon deposits derived from the organic matter in the sulfur.

Repeated analyses of the product have been made. There is some variation from time to time, but in general the analysis (25) is about as follows:

	%
Moisture	0.012
Ash	0.013
H ₂ S	0.001
SO ₂	0.0015
Acidity	0.0035 (as H ₂ SO ₄)
Arsenic	0.0000
Selenium	0.0000
Organic matter	0.000
Purity	99.97

FUTURE PROSPECTS

In plants where it is desired to have a clean stack, it is possible to use a third converter or catalyst stage. Using three stages of conversion with the first operating at 650° to 700° F. to remove carbonyl sulfide, operation of the second and third at about 500° F. will result in a recovery of about 93%. Yield to stack in this case will be virtually free of hydrogen sulfide, and will contain 0.5% or less of sulfur dioxide. This is particularly important in highly populated areas.

Hydrogen sulfide and elemental sulfur fog in stack gases; both of these are dangerous from the point of view of air pollution, but can easily be eliminated by passing stack gases through a simple combustion chamber. Where a stack gas entirely free of sulfur compounds is required or desirable, it is possible to scrub out the remaining sulfur dioxide and sulfur vapor by means of aqueous alkaline solutions—e.g., sodium carbonate or dimethylaniline.

It is probable that leaner gases will draw serious attention in the future. The Mathieson process as described in this paper involves recovery of sulfur from a gas containing about 59% hydrogen sulfide (dry basis). The same process can be used without change for gases containing hydrogen sulfide in concentrations of 20% or higher. In cases where leaner gases are to be treated, a slight modification of the described process can be used, so that there is no chemical limitation on recovery from lean gases. Sulfur can be recovered from any waste hydrogen sulfide gas stream down to very low sulfur concentration; the only limiting factor is economics.

While the quantity of sulfur currently recovered from natural and refinery gases (about 550 tons per day) is a small fraction of the nation's domestic requirements, the continued use of increasingly greater quantities of sour natural gas and crude oil could easily lead to a situation in which recovered sulfur would represent a significant portion of total production. Furthermore, the wider geographical occurrence of sour crudes as compared to natural sulfur deposits will tend to give the recovered product



Sulfur Recovery Plant

Heart of process is in special design of furnace, at left of the control building; parts of waste heat boiler and first sulfur wash tower are in view, and final sulfur tower is shown at right

a price advantage based on location, and in many cases will give a refinery a supply of sulfur in excess of the acid requirements of its operation.

There is considerable activity at present in the field of sulfur recovery. During 1949, the domestic production of mined sulfur was 4,750,000 long tons, and that of sulfur from fuel gases was 70,000 long tons. The recovered sulfur thus accounted for about 1.5% of total domestic production (4).

In addition to Mathieson's two plants, there are now at least 6 other plants in operation or under construction in the United States, each a modification of the process described. Several of these are compared in Table VI. Contracts have been placed for construction in West Texas of a third plant using the Mathieson process, and the Freeport Sulphur Company has completed a plant at the Texas Company's Eagle Point, N. J., refinery.

It is anticipated that with the utilization of more sour natural gas and crude petroleum, and the increasing consciousness of atmospheric contamination, the recovery of sulfur from hydrogen sulfide will take on increasing importance. With this in mind, Mathieson has accumulated process and design data covering a wide range of gas concentrations, and has signed a contract with the Fluor Corporation, Ltd., making Fluor the sole licensing agents for the engineering and construction of sulfur recovery plants incorporating Mathieson's process (5). Within the next few years it is expected that a very significant percentage of our total sulfur demands will be filled with sulfur recovered from hydrogen sulfide.

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PROCESSING EQUIPMENT

- (1A) Babcock and Wilcox, high-chromium iron Croloy.
- (2A) Dean Brothers Pumps, Inc., feedwater pumps and centrifugal cooling water pumps.
- (3A) Foster-Wheeler Corp., standard extended surface economizer with mild steel shell.
- (4A) Lewis, Chas. S. and Co., Inc., *Bull.* 127, acid pumps, Type MT, Form S, size 4.
- (5A) Sutorbilt, positive displacement rotary blower, 22 × 36.



Magnesia-Base Sulfite Pulping

Pulp Thickeners at Weyerhaeuser's Sulfite Pulp Mill, Longview, Wash.

WILLIAM Q. HULL

Associate Editor

in collaboration with

R. E. BAKER

Weyerhaeuser Timber Co., Longview, Wash.

C. E. ROGERS

The Babcock & Wilcox Co., Alliance, Ohio

IN THE world's first sulfite pulp mill, constructed by the Swedish chemist, C. D. Ekman, at Bergvik, Sweden, in 1874, magnesium bisulfite was used for a period of time as a base for the preparation of the cooking acid (1). As the process developed and came into general use, however, limestone was almost universally adopted because of its widespread availability and low cost. In relatively recent years magnesia-base pulping has again received serious consideration and the first full-scale commercial plant utilizing the process is in operation.

The sulfite process is second only to kraft as a source of chemical wood pulp; production by the sulfite process in the United States in 1950 was approximately 3,000,000 tons (Table I). Its origin is generally attributed to the efforts of Tilghman, who was granted a patent in 1876 entitled, "Treating Vegetable Substances for Making Paper Pulp" (10). Tilghman originally proposed lead-lined, cylindrical vessels as digesters and numerous

mechanical difficulties resulted. Ekman, presumably unaware of the Tilghman patents, equipped his mill with small rotating digesters heated indirectly by means of steam jackets. During this same period, A. Mitscherlich developed a process in Germany using horizontal, stationary cylindrical digesters, indirectly heated by coils of lead pipe, in the place of Ekman's rotating vessels, and Eugene Ritter and Carl Kellner, in Austria, operated mills in which steam was admitted directly into the cooking vessel. The first sulfite mill in the United States, built by Charles S. Wheelwright in East Providence, R. I., was based on Ekman's work. A few years later, in 1887, the first Mitscherlich mill in this country was constructed in Alpena, Mich.

Today, chemical pulp is made by three basic processes—kraft, sulfite, and soda. In later chapters of this book, the history and manufacture of kraft pulp and paper are described in detail, and a comparison of process and product characteristics of the three

TRADE GLOSSARY

Total sulfur dioxide: Total SO_2 , determined by titration according to TAPPI Standard T-604m, expressed as per cent total SO_2

Free sulfur dioxide ("available" SO_2): Sum of actual free SO_2 plus one half the SO_2 combined as bisulfite, determined by titration according to TAPPI Standard T-604m, expressed as per cent free SO_2

Combined sulfur dioxide ("nonavailable" SO_2): SO_2 combined with base as monosulfite, determined by difference of free SO_2 and total SO_2 , expressed as per cent combined SO_2

Sulfur dioxide: SO_2 gas made by burning sulfur or pyrites with sufficient air to form SO_2

Bisulfite liquor base: Magnesium oxide used in preparation of bisulfite cooking liquors

System or finished acid: Bisulfite liquor prepared by combination of SO_2 and base in presence of water, with excess of SO_2 in solution

Storage acid (also known as raw acid): System acid in reserve for transfer to acid accumulators for fortification by injection of additional SO_2

Accumulator acid: Storage acid held in pressure vessels during fortification by SO_2 in digester-relief gas

Cooking liquor: Accumulator acid ready for use in the digester cooking operation, after fortification is completed

Digester liquor: Cooking liquor as it exists in digester at various stages during progress of cooking operation

Digester top relief: Gas withdrawn from top of digester during early stage of cooking operation and returned to accumulator to conserve SO_2 and heat

Digester side relief: Digester liquor withdrawn by side relief from upper section of digester in early stages of digestion and returned to accumulator or storage to conserve SO_2 and heat

Digester on-side test: Test of digester liquor for total, free, and combined SO_2 just before digester is put on side relief

Digester off-side test: Test of digester liquor for total, free, and combined SO_2 just after digester is taken off side relief

Digester blow-down test: Test of digester liquor for total, free, and combined SO_2 at beginning of pressure-relief period toward end of digestion

Digester dump test: Test of digester liquor for total, free, and combined SO_2 just before digester is dumped

Sulfite waste liquor or red liquor: Spent liquor from sulfite digestion (containing dissolved constituents of wood) removed from pulp as digester is dumped

Weak red liquor: Sulfite waste liquor (approximately 15% solids) which is further concentrated in cascade and multiple effect evaporators

Strong red liquor: Sulfite waste liquor (60% solids), which has been through evaporators

Sulfur consumption: Pounds of sulfur (from elemental sulfur, pyrites, or SO_2) consumed per ton of air-dry pulp, determined from operating and inventory records

Magnesium oxide consumption: Pounds of base material consumed per ton of air-dry pulp, determined from operating and inventory records

basic methods of chemical pulp making is given (7, 8). This article describes the manufacture of pulp by the sulfite process and more especially sulfite pulping in which magnesium oxide is used as the base of the cooking liquor.

ECONOMICS OF SULFITE PULPING

All chemical pulp making involves the separation of cellulose, which serves as raw material, from the unstable and unwanted lignin and other noncellulosic components of the wood. In the kraft process, a mixture of sodium hydroxide and sodium sulfide is used to dissolve noncellulosic materials from the wood. The soda process depends on the dissolving action of sodium hydroxide alone. The sulfite process differs from these alkaline processes in attaining the same action with an acid cooking liquor.

The more common sulfite process consists of the digestion of wood, which has been reduced to chips, in an aqueous solution containing calcium bisulfite, $\text{Ca}(\text{HSO}_3)_2$, and an excess of sulfur dioxide at temperatures from 130° to 150° C. In order that the chips be completely impregnated with cooking liquor, the temperature is raised slowly during the first few hours of the cook. A cooking time of from 7 to 12 hours is required. The pulping process involves two principal types of reactions, which are probably concurrent: the reaction of the lignin with the bisulfite and the hydrolytic splitting of the cellulose-lignin complex (9). Hemicelluloses are hydrolyzed to simpler soluble compounds, and the extraneous wood components are also acted on. Not dissolved is

the resistant cellulose, which actually is sulfite wood pulp. This is separated from the cooking liquor and processed into a finished pulp product. The cooking liquor is prepared from sulfur dioxide gas (obtained from burning sulfur), which is absorbed in water in the presence of limestone to form calcium bisulfite.

The cellulose content of various woods in the United States ranges from 51 to 65% (4), and since this is the primary constituent that is desired in the end pulp product, it follows that approximately half of the wood charged is dissolved by the cooking liquor. The composition of the dissolved fraction varies with the specific process used, but, generally, the chief organic components are modifications of lignin and the more readily dissolved carbohydrates and their modifications. The by-product liquor resulting after the separation of the cellulose is called sulfite residual liquor or red liquor. It has been estimated that for every ton of sulfite pulp produced, there result 2000 gallons of the waste liquor containing 12% solids (5). Of the solids, as much as 65% is lignosulfonic acid; 20%, reducing sugars; 8.4%, sugar-sulfur dioxide derivatives; and 6.7%, calcium. The composition varies and depends on the wood used and cooking conditions.

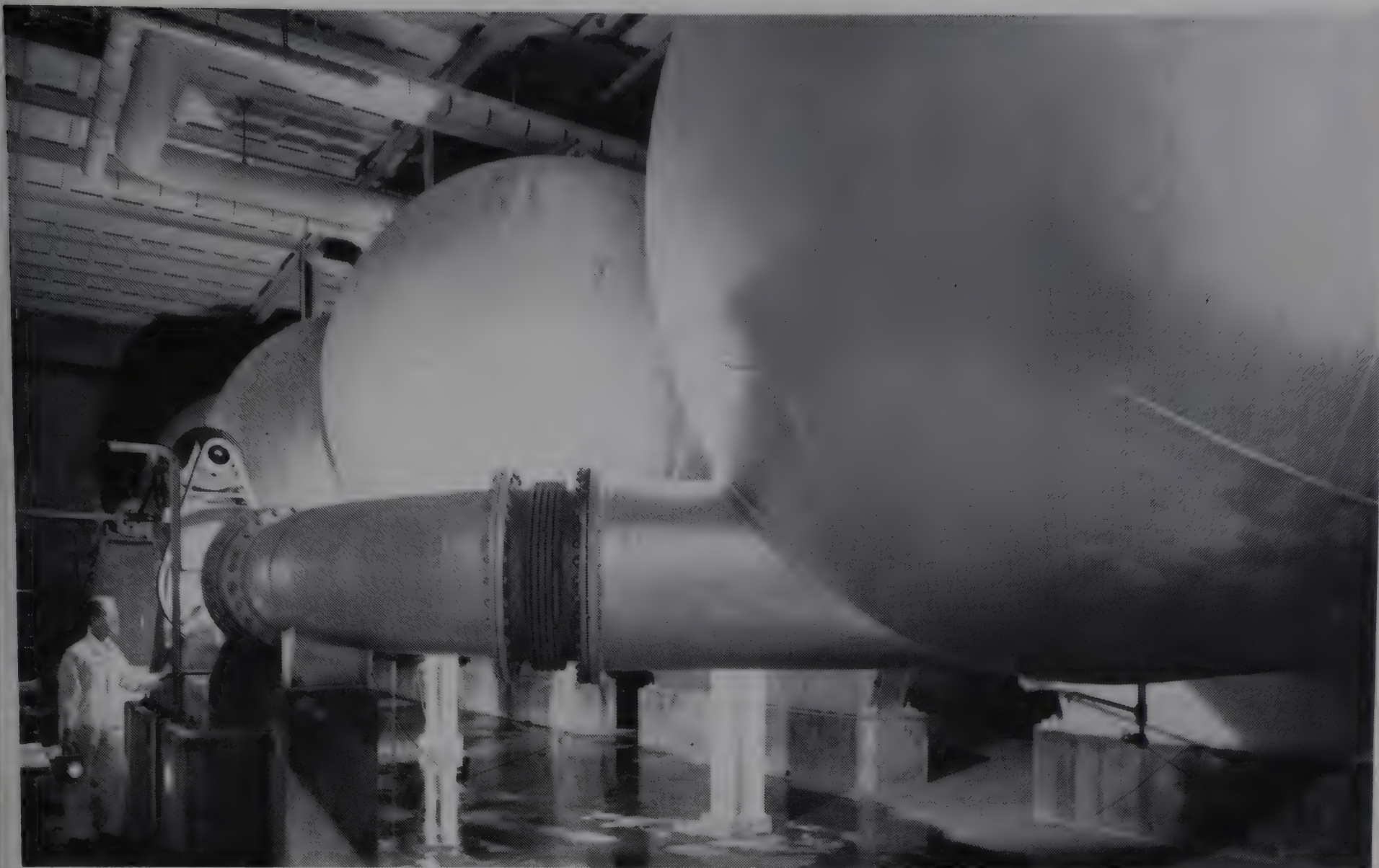
In the United States and Canada, about 4,000,000 tons of sulfite pulp are produced annually. Consequently, the volume of waste liquor is enormous, and the dissolved components of the wood weigh approximately 4,900,000 tons. The disposal of this vast amount of organic matter has become a problem in nearly every area where sulfite pulp is produced, particularly because some of the sugars and organic acids become consumers of oxygen and thus pollute streams into which the waste liquor is directed.

During the past 15 years interest in the disposition of sulfite waste liquor has been stimulated considerably by public reaction and industrial and legal efforts to eliminate stream pollution of all types. Since more than half of the raw material entering the pulping process appears in the waste liquor as dissolved organic solids, the economic aspect has also encouraged extensive study. Investigations of the waste liquor problem have thus followed two lines of endeavor—disposal and utilization.

In order that there be relatively little decrease in the dissolved oxygen content in waters into which sulfite waste from mills is

TABLE I. U. S. SULFITE PULP PRODUCTION (13)

Year	Thousand Short Tons		
	Bleached	Unbleached	Total
1941	1703	1216	2919
1942	1717	1213	2930
1943	1553	883	2436
1944	1523	863	2386
1945	1544	816	2360
1946	1692	784	2476
1947	1902	894	2796
1948	1909	902	2811
1949	1829	707	2536
1950	2111	744	2855



Pulp Dump Tanks

Four of these tanks, 70 feet long and 17 feet in diameter, are used in pairs

discharged, waste liquor disposal has had as its objective the reduction of the biological oxygen demand of the waste liquor. Included in these studies have been the use of trickling filters, re-aeration, or chemical alteration of the carbohydrate portion of the liquor. All these methods require equipment, power, and maintenance and result in a higher cost of the pulp produced.

None of the suggested treatments seeks to recover the carbohydrate portion of the waste liquor. Utilization of the solids in the waste liquor has been approached by many who have endeavored to convert the organic material into useful chemical compounds or to extract from the liquor, by precipitation or other means, the lignin or carbohydrates in such a manner that they will find commercial outlets. Varying degrees of success have resulted. Among the principal products which have been investigated or proposed are alcohol by fermentation of the waste liquor; yeast produced by the fermentation process; vanillin from the lignin present; oxalic acid; tanning material; road binders; special cements; portland cement accelerator; core-binders; and plastics from the lignin present. A recent report in this series described the production of food yeast from sulfite liquor (3).

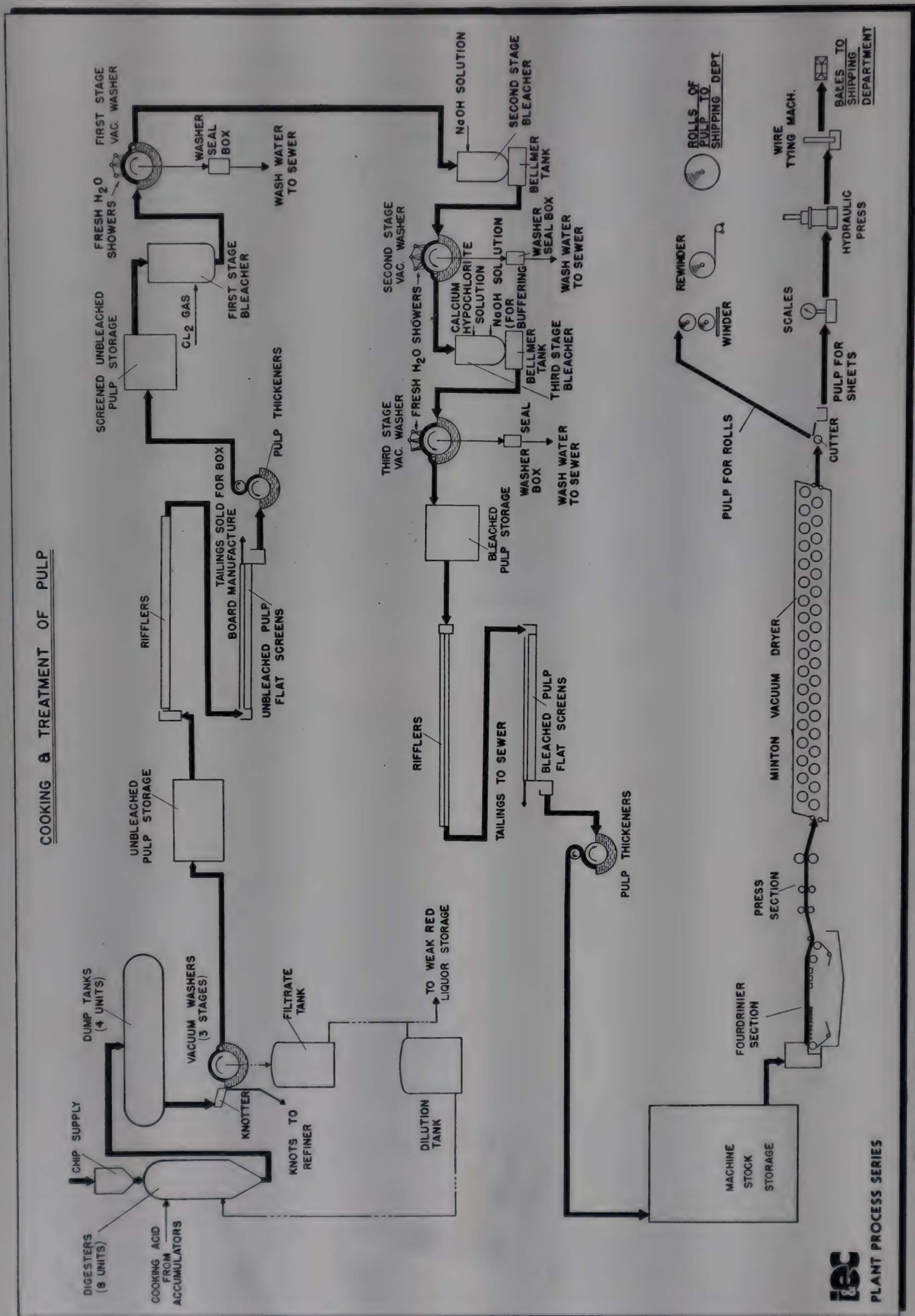
Another important consideration is the heat value of the dry organic solids in the waste liquor which ranges between 7000 and 8000 B.t.u. per pound. This material, under proper conditions, offers a valuable source of energy, in the form of fuel, which might be supplied to convert wood into chemical pulp. Some years ago, it was realized that if, in the process of utilizing the organic solids as a source of energy, it was possible to recover the chemicals used for producing the pulp, there would result a cyclic process in which all of the resultant products could be utilized by the pulp manufacturer. Attempts to develop such a process brought forth numerous proposals to evaporate the sulfite liquor from calcium-base pulping and use the concentrated liquor as fuel. Approximately 9000 to 10,000 pounds of steam can be produced from the

waste liquor resulting from the production of 1 ton of sulfite pulp. However, these proposals were not particularly attractive except as a means of waste liquor disposal because the digesting chemicals are not recovered in a form to permit their re-use in the process. Calcium and sulfur are recovered as calcium sulfate, and as the calcium sulfate cannot be broken down into calcium oxide during the use of the concentrated liquor as a fuel, its recovery as a cooking chemical is not possible.

Sodium and ammonia have been substituted for calcium as a pulping base and are used in a limited number of commercial plants. However, the recovery of the bases as usable chemicals for the sulfite pulping process is complicated and costly.

About 1936, Tomlinson of Howard Smith Paper Mills, Ltd., found that, contrary to the generally accepted view, when a pure magnesium-base liquor is burned, magnesium sulfate did not reduce to the sulfide in the presence of carbon, but instead had the unique characteristic of reducing to the oxide with the liberation of sulfur dioxide. When the liquor is burned under certain furnace conditions, the oxide produced is exceedingly reactive in combining with sulfur dioxide. He also found that the magnesia-base liquor could be evaporated to high concentrations with comparative freedom from insoluble scale formation. These discoveries are the heart of the cyclic magnesia-base process of pulping wood by the sulfite method (11).

The first pilot plant to make pulp by the new cyclic process was installed as a joint venture by the Howard Smith Paper Mills, Ltd., and The Babcock & Wilcox Co., in 1937 at the Cornwall, Ont., mill of Howard Smith. In 1940 these companies announced the results of several years of joint experimental work and pilot plant operation of the magnesium oxide cyclic process (12). At about the same time, Weyerhaeuser Timber Co. was independently developing the same process, and a pilot plant was operated at the company's Longview, Wash., plant. A commercial digester was satisfactorily operated for about a year using



magnesium-base acid, with recovery in a pilot plant furnace. The results of this pilot plant operation have been published (2).

Inasmuch as the three companies had common objectives in developing the magnesia-base process and in order to eliminate further duplication of effort, a cooperative arrangement was worked out by which all the experience gained in the several pilot plant operations and earlier research would be utilized in the conversion of a single commercial sulfite mill. An efficient and economical answer to the utilization of sulfite waste liquor could then be offered to the pulp industry. The Longview, Wash., mill of Weyerhaeuser Timber Co. was selected as the first mill to be converted to the magnesia-base process. It is one of the three branches of Weyerhaeuser's pulp division, which also operates a sulfite pulp mill at Everett, Wash., and sulfate pulp mills at Springfield, Ore., and Longview.

LONGVIEW, WASH., MILL OF WEYERHAEUSER TIMBER CO.

The sulfite pulp mill at Longview produces approximately 275 air-dry tons of pulp every 24 hours. Annual raw materials required for production of this output are shown in Table II. Pulpwood is chiefly hemlock (85%) and white fir (15%) which is grown at the company's St. Helens' tree farm in southern Washington, a part of Weyerhaeuser's 2,000,000 acres of timberland. Logs are brought by rail to Longview, where they are dumped into the Columbia River adjacent to the mill site for convenience in handling and sorting. Log ponds are provided for species of wood to be used in the various operations. A typical sawmill log haul lifts the logs from the water, and the logs are sawed to 24-foot lengths by a circular saw.

A chief requirement of quality in the production of pulp is that it be substantially free from dirt, particles of bark, and other objectionable matter. Thus logs must be completely cleaned of bark before processing. At Longview, this operation is performed by a hydraulic barker. The development of the hydraulic log barker during World War II by Weyerhaeuser introduced new economies in wood utilization and has now been adopted by many mills on the West Coast. The barker is of the chain-rotating type. As logs are rotated at a speed of approximately 4 r.p.m., water, at 1400 pounds per square inch, is applied through jets mounted on a traversing carriage moving at a maximum speed of 50 feet per second in the lengthwise direction of the log. Approximately 900 gallons of water per minute are used. After the log has been rotated one complete revolution, the barking nozzles are forced into a small end chamber out of contact with the log. The log-turning chain and supporting arms are lifted from the log, which is then ejected by an unloading mechanism. At this point, a new log is fed into the barker and the process repeated. One pass of the jet stream usually removes all the bark, but any that remains



Cascade Evaporators and Multiclone Separators

Operator is adjusting gate valve through which recovered MgO passes into screw conveyor

is removed by men called "spudders." Logs above 40 inches in diameter are reduced by band saws before further processing. Prewar barkers were broadly of two types—rotating knife barkers and drum barkers; the former is rapidly becoming obsolete. From the hydraulic barker, the bark is sent to a waste heat furnace, and the barked logs are ready for further processing.

In order that the cooking liquor may penetrate the wood quickly, completely, and uniformly, pulpwood must be reduced to chips for chemical pulp manufacture. This procedure is known as chipping and produces wood sections of uniform size, usually about $\frac{5}{8}$ to $\frac{3}{4}$ inch wide and $\frac{1}{8}$ inch in thickness. Pulpwood blocks from barking machines or storage which have been accepted as "clean" are fed directly to the chipper for this operation.

At Longview, logs are fed at a rate of 1 foot per second from a conveyor by sliding them lengthwise down an inclined chute and into the chipper spout. The wood is supported by a bed knife and chipped off as it comes into contact with four knives in a revolving steel disk, 170 inches in diameter and 7 inches thick; the disk is rotated by a 1500-hp., 240-r.p.m., synchronous motor. Average chip size is $\frac{13}{16}$ inch. In other installations, chippers with 8, 10, or 12 knives are in general use. Chips are screened for removal of slivers, knots, and fines and are conveyed by a rubber conveyor (30 inches wide and $\frac{3}{8}$ mile long) to a chip storage building which has a capacity of 1895 air-dry tons of chips, equivalent to approximately 50 cooks.

The manufacture of pulp by magnesia-base pulping can be briefly summarized: Chips prepared as described are cooked in an acid liquor. Lignin and other noncellulosic materials are dissolved during the cooking or digesting step by the active cooking chemicals—magnesium bisulfite and sulfur dioxide in aqueous solution. The nondissolved material is practically pure cellulose and is separated from the liquor on vacuum washers; after screening and bleaching it is subsequently processed into pulp sheets (Figure 1).

TABLE II. APPROXIMATE ANNUAL REQUIREMENTS, WEYERHAEUSER'S SULFITE MILL

Water, millions of gallons	6,432.4
Sulfur, tons	5,000.0
Magnesium oxide, tons	2,500.0
Chlorine, tons	4,600.9
Sodium hydroxide, tons	2,228.4
Lime, tons	855.7
Wood, air-dry tons	225,000.0

The balance of the process is concerned with recovery and re-use of the chemicals used in digesting the wood. The sulfite residual liquor or red liquor recovered as filtrate from vacuum washing the pulp is evaporated to 55 to 60% solids in multiple-effect evaporators and burned in a special furnace. In the incineration of the liquor, heat is created for the boilers and magnesium oxide and sulfur dioxide are formed and leave the furnace with the flue gas. The highly reactive magnesium oxide is collected in multiclones and conveyed to absorption towers, where it is re-used in making cooking liquor. Sulfur dioxide gas from the furnace is cooled and fed into the bottom of the towers; magnesium oxide, as a water slurry, is fed to the top of the towers. The acid is fortified to standard strength with make-up sulfur dioxide obtained from the burning of sulfur.

Cooking

There are eight cookers or digesters at the Longview mill (9E). These are large cylinders, 6400 cubic feet each, equipped with conical bottoms and bell tops. The digesters are fabricated from 1-inch mild steel plate and have a double acid-resisting brick lining; over-all height is 52 feet and diameter is 16 feet. The rated capacity of each digester is 16 tons of air-dry pulp per cook. Each digester is equipped with an indirect steam heater (3E) to prevent dilution of the waste liquor with steam condensate. These single-pass tube heaters are made of Type 316 stainless steel, with a total heating surface of 450 square feet per heater; steam is used at 125 pounds per square inch gage and 410° F. Steam requirements for pulp digestion and other processing steps are shown in Table III.

Wood chips are carried by a belt conveyor to a 42-inch filling belt over the digesters. The filling hopper can be moved from digester to digester for charging. A charge consists of approximately 62 tons of chips (47.8% water), which is fed through the top of the digester. The head is then bolted down and pulp sheets are used as gasket material. The "hot acid" or Chemipulp process is used: Acid at 65° C. is fed into the digester from the acid accumulator at a ratio of 4.0:1 of oven-dry wood charged. Total acid to a digester is approximately 21,000 gallons. Red liquor at 160° F. is added to fill the digester. Approximately 6000 to 7000 gallons are required. Cooking acid compositions at various points in the process are shown in Table IV.

Cooking liquor is circulated through the heater and digester by a centrifugal pump (4000 gallons per minute) driven directly by a 75-hp., 2200-r.p.m., 2200-volt motor. Collector rings or strainers, made of Type 316 stainless steel, with $\frac{5}{16}$ -inch holes spaced $\frac{19}{32}$ inch between centers, are located at the bottom of the



Turbine Room

Two noncondensing turbines and 6250-kv.a. generators

cylindrical section of the digester. The circulating liquor passes through the strainers and heaters, and then the flow is divided; 25% goes to the bottom digester fitting and the remainder, through a header ring, to three spray nozzles at a point near the top of the digester.

At the end of 3.5 hours, the temperature reaches 139° to 140° C., and the pressure is approximately 90 pounds per square inch. Steam to the circulating system is cut off just before the maximum temperature is reached. At this point, cooking liquor is relieved by side relief to the accumulator to a level of 13 feet from the top of the digester. This decreases the quantity of liquor that must be removed from the pulp later and provides gas space for later "gassing off" or relief of sulfur dioxide and steam to the acid-fortifying system. At the end of 7 hours the circulation of the cooking liquor is stopped and digestion is almost completed.

Dumping and Washing

A departure from the conventional practice of blowing a digester into pits is practiced in this particular magnesium oxide plant. When the cook is completed, the pressure is relieved to near atmospheric. This is done in two steps: From 90 to 35 pounds per square inch, the pressure is relieved into the accumulator; from 35 pounds per square inch to as near as possible to atmospheric, it is relieved to the acid storage tanks after being passed through a single-pass, indirect heat exchanger. An eductor is used to shorten the time required to relieve the digester to zero pressure, and approximately 20 minutes are required for this additional relief. The digesters are connected to a common header and the stock is flushed out by back-filling with red liquor and pumping. Red liquor is pumped to the suction side of the digester circulating pump and can be diverted to the bottom, top, or collection ring section of the digester. In the flushing or dumping step, the pulp is diluted to approximately 3.5% air-dry consistency. A trap, commonly called a "brick catcher" is in the flow line between the digesters and the dump tank. The brick catcher removes any particles which the pulp may have picked up from the lining of the digesters.

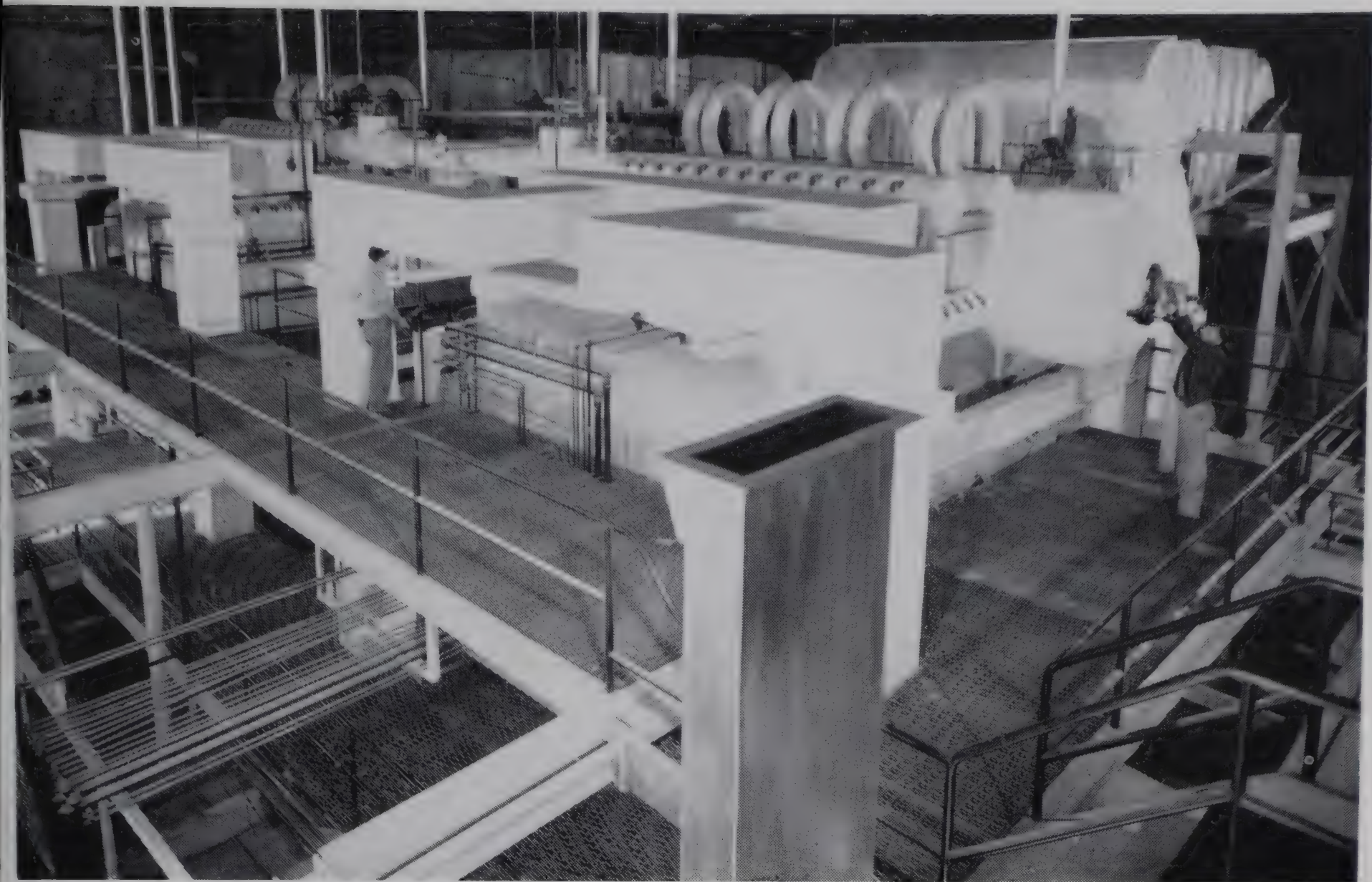
The 70-foot steel dump tanks, which are connected and used in pairs, are of unusual design and novel appearance. The tanks are set at a slope of $\frac{7}{32}$ inch per foot, the low end being 3 feet above

TABLE III. STEAM REQUIREMENTS

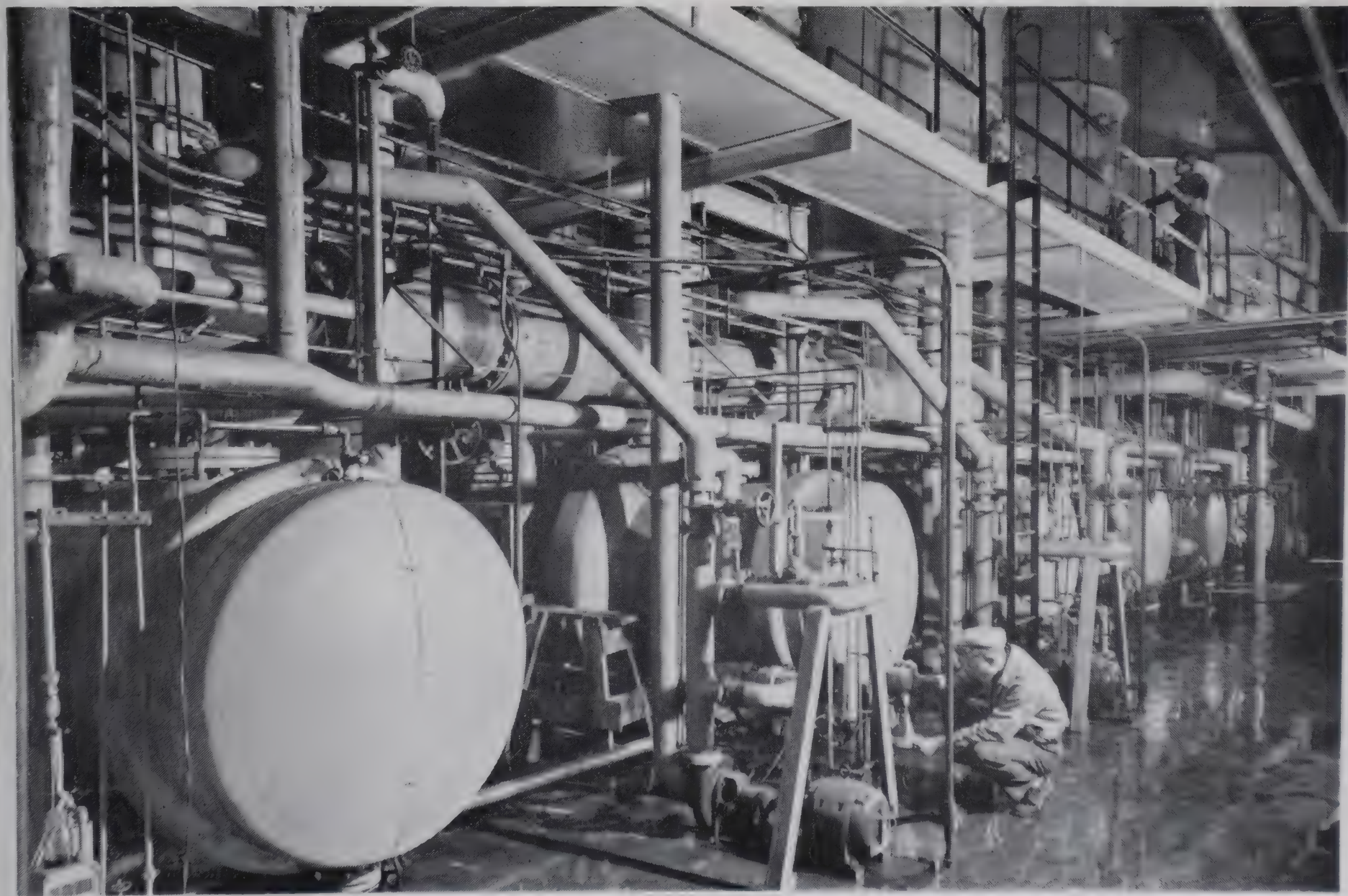
Use	Steam Used/Ton Air-Dry Pulp, Lb.	Pressure, Lb./Sq. Inch	Temp., ° F.
Red liquor evaporation	3200	40	320
Pulp digestion	3200	125	416
MgO furnace operation	850	40	320
Bleach plant	1175	125	416
Pulp dryer	3150	35	
Wood barker	1000	125	416
Misc. (acid making, heating, auxiliary equipment)	100	125	416
Steam generated in waste heat boiler of MgO recovery furnace	7800	620	720

TABLE IV. TEMPERATURES AND TYPICAL COOKING ACID ANALYSES

	Sulfur Dioxide, %			Temp., ° C.
	Total	Free	Com- bined	
Furnace gas absorption tower	4.60	2.30	2.30	31
Fortified raw acid	5.75	3.50	2.25	32
Storage tank acid	6.50	4.50	2.00	36
Low pressure accumulator	8.40	6.50	1.90	50
High pressure accumulator	8.60	7.00	1.60	65



Top Level View of Heat and Chemical Recovery Furnace



Sulphite Quintuple Effect Evaporator

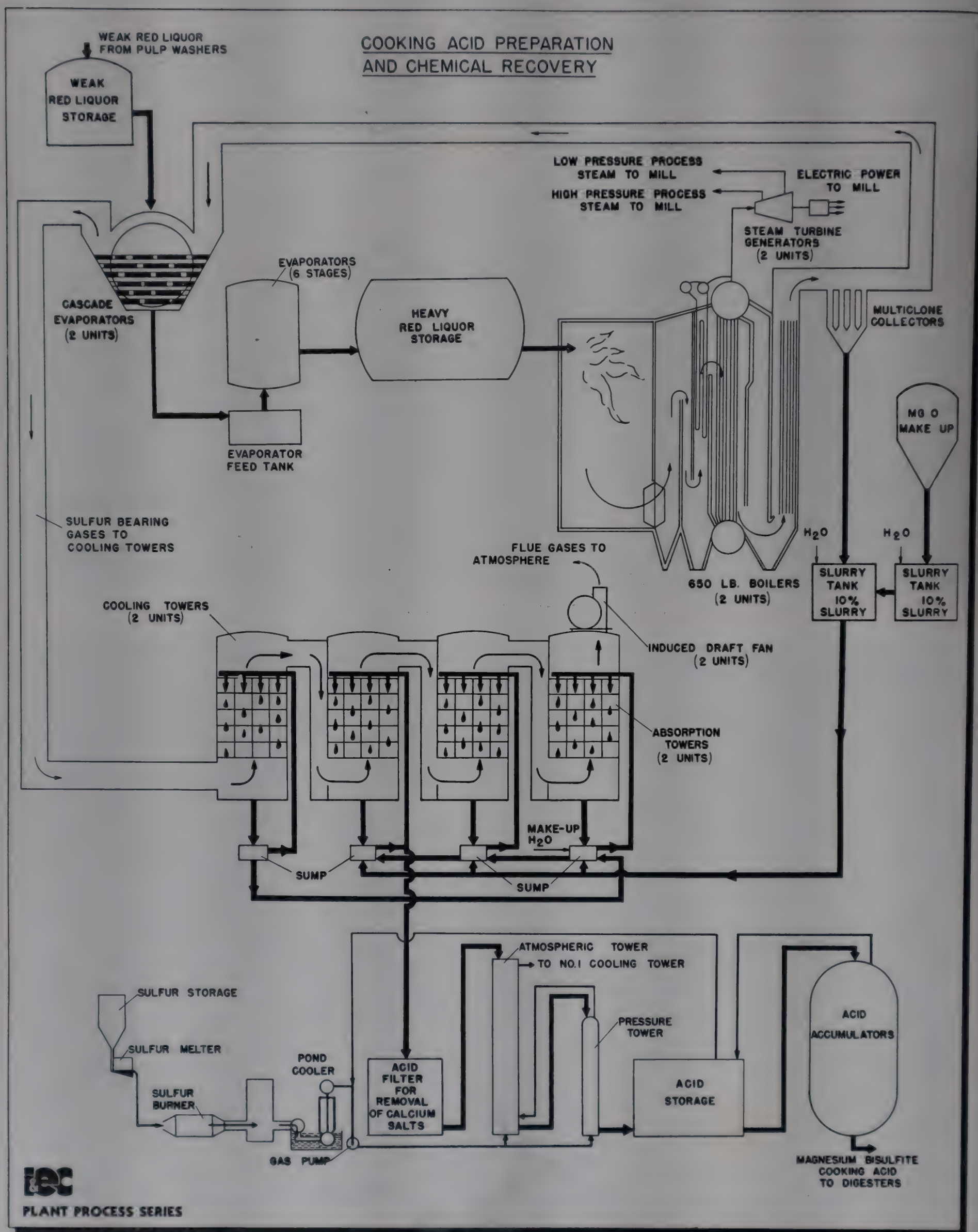


Figure 2. Flow Sheet for Preparation of Cooking Acid and Recovery of Chemicals in Magnesia-Base Pulping Process



MgO Sulfite and Kraft Mills at Longview, Wash.

Tall unit is acid fortification tower; center buildings are MgO recovery plant

floor level. Each pair of these tanks provides capacity of 183,000 gallons; circulation is provided by 500-r.p.m. pumps operated by 20-hp., 550-volt motors with V-belt drive. The pulp is pumped from the dump tanks by a centrifugal pump (2300 gallons per minute) operated by a 40-hp., 550-volt, 1800-r.p.m. motor.

In the dumping step, only 5 to 10 pounds of sulfur per ton of pulp flash off as sulfur dioxide gas. Even though the pressure at the time of dumping is very nearly zero, the static head on the digester prevents relieving all the free sulfur dioxide. Also, it is not possible to obtain good circulation at the latter part of the cooking cycle. This sulfur dioxide is recovered by venting the dump tanks to the furnace flue gas absorption system.

Some of the early proposals for the magnesium oxide process indicated that ratios as low as 2.5 pounds of total liquid per pound of oven-dry wood could be used satisfactorily (6). At the present time, the ratio has been reduced from 5.1:1 (calcium-base pulping) to 4.0:1, and the reduction thus far saved 6000 to 7000 gallons of cooking acid per digester charge. Ratios between 2.5:1 and 3.5:1 are still considered as practical for future operations, and additional savings in cooking liquor and consequently steam for cooking and evaporation will be realized.

Prior to washing, the pulp is freed of knots by four 3 × 4 foot vibrating knotters operated in parallel (2E). Screens are constructed of $\frac{3}{16}$ -inch Type 316 stainless steel and openings are $\frac{3}{8}$ inch in diameter. The stock is assisted through the screen plate by vibration of the screen frame. Oversize material, knots, etc., retained by the screen are carried to the discharge end of the screen frame and dropped into a tailings trough. No attempt is made to recover the residual waste liquor in the knots since the quantity is small. Knots and oversize particles of pulp are defibered and mixed with screenings and sold for boxboard manufacture.

Material passing through the $\frac{3}{8}$ -inch openings is ready for

washing and filtering and passes by gravity to a three-stage vacuum washer. Three 8 × 16 foot stainless steel vacuum washers, set in concrete vats with acid-resistant tile linings, are used (7E). The piping arrangements and liquor circulating systems are similar to a conventional brown stock washing system normally used in a kraft mill. The effluent from the third stage is pumped and sprayed on the pulp mat of the second stage; the effluent from the second stage is sprayed on the first-stage pulp mat. Temperature is maintained at approximately 180° F.; vacuum on drums is 3 inches of mercury. The filtrate from the washer, containing about 14 to 15% solids, goes to the weak red

TABLE V. LONGVIEW MILL PRODUCTION CONTROL DATA

(All tests by TAPPI standards or modifications)

	Pulp Grade		
	Papermaking	Nitrating	Absorbent
Per cent of total production	80	10	10
Chemical testing of pulp, %			
Alpha cellulose	90.2	92.9	91.2
Beta cellulose	1.4	1.9	2.4
Gamma cellulose	8.4	5.2	6.4
Ash	0.15	0.12	0.09
Fe	0.0003	0.0004	0.0004
Cu	0.0005	0.0005	0.0006
Ca	0.09	0.06	0.06
Si	0.006	0.006	0.005
Ether-soluble extractives	0.35	0.32	0.28
Alcohol-soluble extractives	0.04	0.02	0.04
Total pitch	0.39	0.34	0.32
Copper No., Schwalbe-Hagglund method	1.5	1.2	1.6
10% KOH solubility, %	13.3	11.6	15.8
Viscosity, centipoises	247	135	134
Physical testing of sheets			
Brightness, % on G.E. instrument	88.0	88.0	88.0
Bursting strength (Mullen), lb./sq. inch/unit wt. × 100	135	110	120
Aggregate tear, Elmendorf units/basic weight	1.6	1.9	1.6
Fold endurance	600	400	500

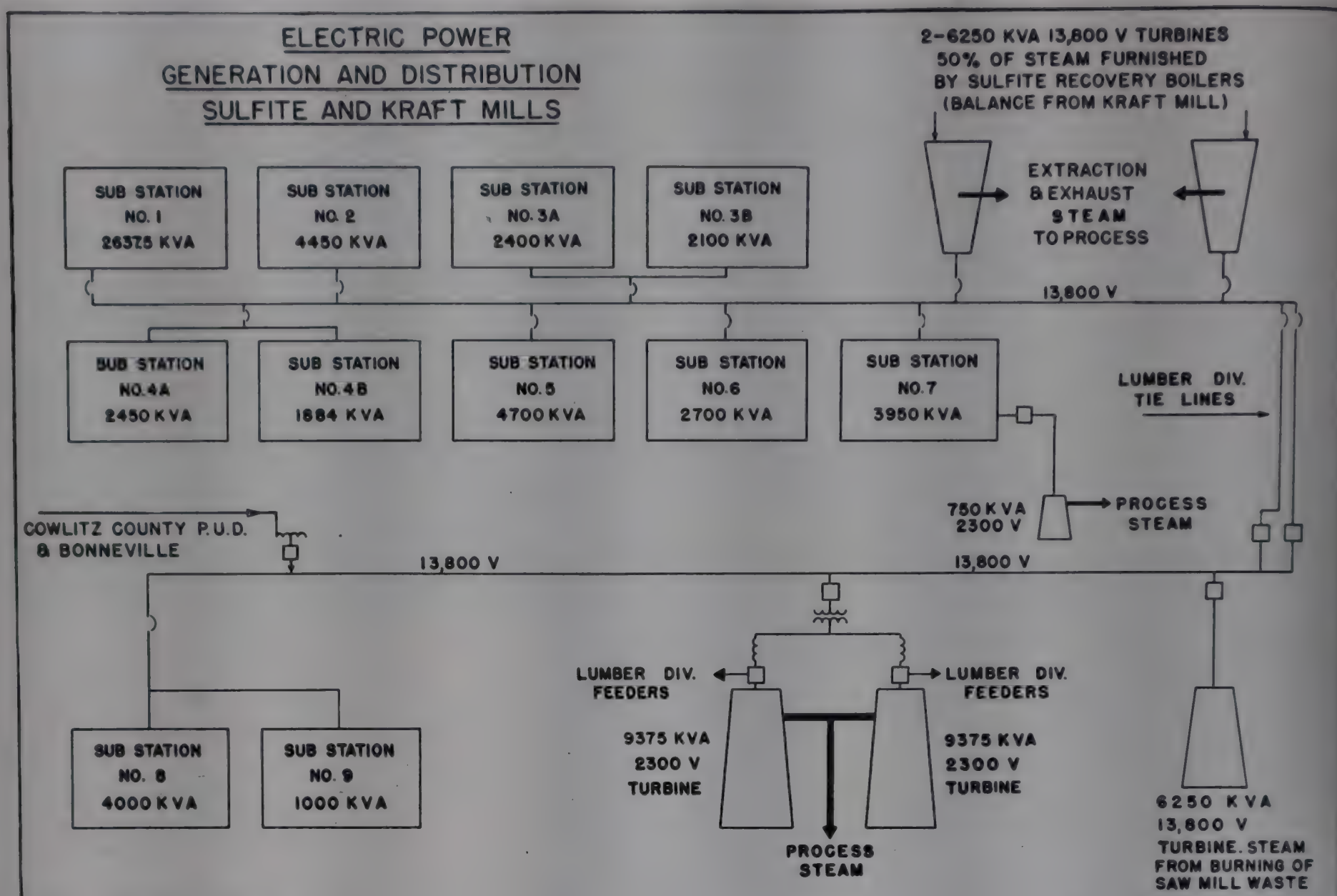


Figure 3. Electric Power Generation and Distribution at Longview Mill

liquor storage tank for subsequent evaporation. The washed pulp at approximately 3% air-dry consistency goes to the unbleached pulp storage tank. This is a 140,000-gallon wood stave tank, 36 feet in diameter and 18.5 feet deep.

A foam tank and foam breaker were installed in anticipation of foam occurring as in kraft pulp washing. However, very little foaming has been encountered, and at no time has foam carried over from the washer foot tanks. There are five additional stock tanks maintained for standby use and storage. These are similar to the unbleached pulp tank. A 282,000-gallon cylindrical wood tank is also used for standby and as a mixing tank when needed.

The pulp is further processed into one of three grades of finished pulp product as shown in Figure 1; the properties of these pulps are listed in Table V.

Evaporation

Before the weak red liquor can be ignited and burned in the recovery furnace, with subsequent recovery of cooking chemicals, it must be freed of a part of its water content. This is done in two stages: It first passes through two cascade evaporators, which increase the oven-dry consistency from 15 to 17% (6E). These cascades, of the single-wheel type, are 12 feet in diameter with 8-foot 7-inch faces. They are located in the furnace gas stream between the multiclone separators, where magnesium oxide is recovered, and the gas cooling towers (Figure 2). Originally, the red liquor was first passed through the multiple-effect evaporators and then to the cascade evaporators for further concentration and consequent cooling of the recovery furnace gases before being fired in the recovery furnaces. However, this cycle resulted in the formation of foam and calcium sulfate scale in the cascades and caused interruptions in the fuel supply to the recovery furnaces. To prevent these occurrences, the liquor cycle was changed to pass the weak liquor from the washers through the cascades for initial concentration and finally to the multiple-effect evaporators.

In the multiple-effect evaporators, the weak red liquor is concentrated to approximately 60% solids. A six-body quintuple-effect evaporator is used (4E). Outside heat exchangers and forced circulation are used to provide high tube velocity and to cut down on heating surfaces. Stainless steel or stainless steel-clad construction was used throughout the evaporation unit. Tubes are 1 inch in diameter and 12 feet long. Each heater has 1460 tubes or 4000 square feet of area. Red liquor enters the evaporators at 168° F. and leaves at 250° F.

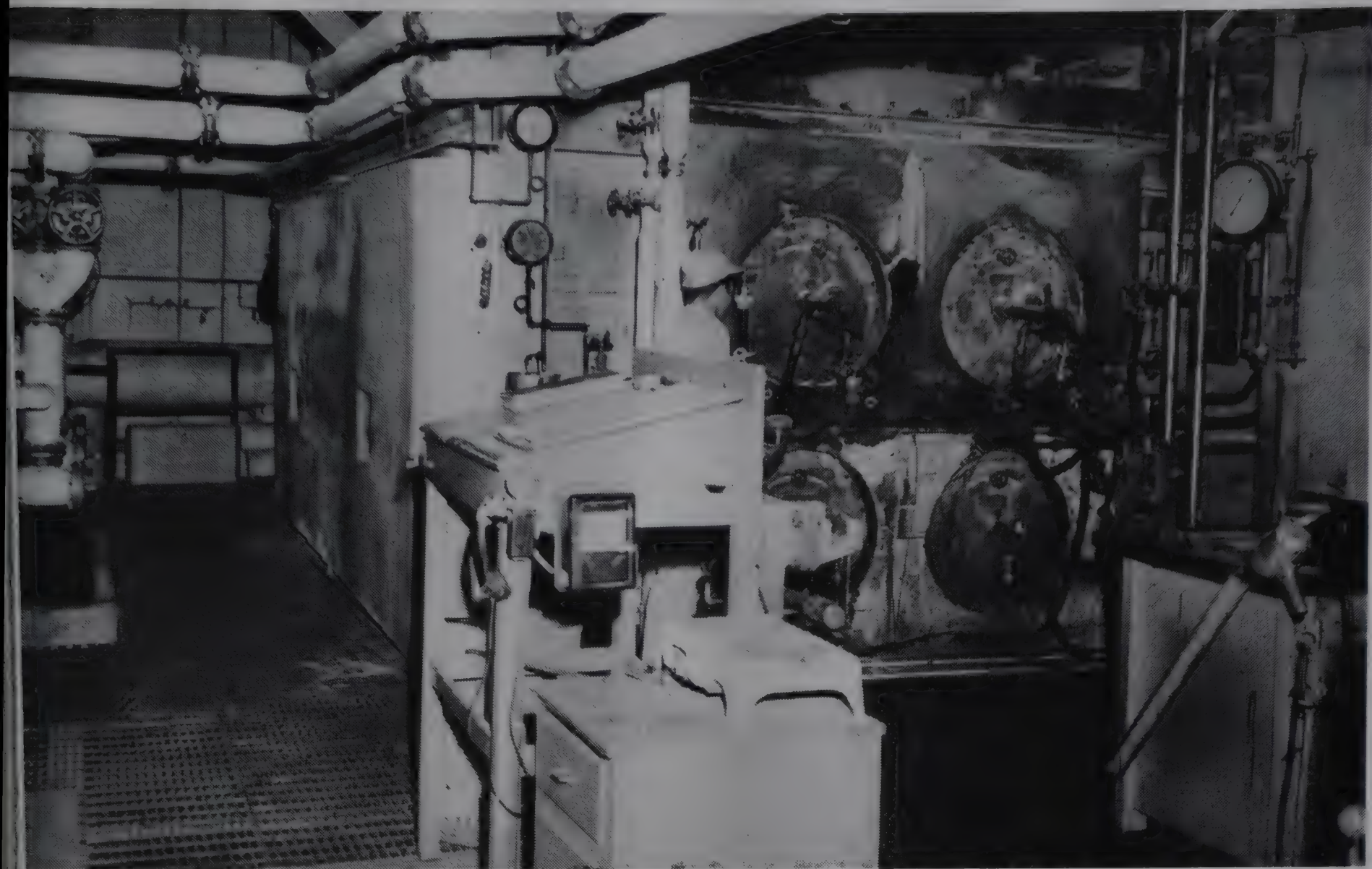
The evaporators are designed to produce 4.58 pounds of evaporation per pound of steam. Pounds of water evaporated per pound of steam used has actually been 3.25 because the unit is being operated temporarily as a quadruple effect with three first effect bodies for greater capacity. Weak red liquor is introduced into No. 2 effect, and the flow is concurrent with the vapors through Nos. 2, 3, and 4. The liquor then is transferred through 1C, 1B, and 1A.

A spare heating element and circulating pump are provided since it was anticipated that some difficulties would be experienced with scaling of heating surfaces. Scale formation was aggravated by abnormally high magnesium sulfate formation during preliminary operations when the rate of burning of liquor and sulfur was such that high quantities of excess air were admitted to the acid plant absorption system. During more stable operation, however, the quantity of sulfate formed is more uniform and of a smaller amount, and it is possible to operate the evaporator unit consistently at system rate.

The concentrated or strong red liquor goes to a storage tank and is ready for burning in the specially designed magnesium oxide recovery furnace.

Burning

Two furnaces used for the actual burning and chemical recovery in the magnesia-base pulping cycle are each attached to



Firing Deck of MgO Recovery Furnace

boilers of the two-drum Stirling extended furnace type, equipped with gas air heaters and rated as 137.5-ton recovery units (1E). These units are rectangular in shape, $50\frac{1}{2}$ feet long by $18\frac{1}{2}$ feet wide and 38 feet in height. Each is designed for the production of 69,600 pounds of steam per hour at 615 pounds per square inch and 725° F. The strong or heavy red liquor is fed into the furnace, at the second floor level, through four steam atomizing Y-jet burners on each side of the furnace and forced draft air at 750° F. for combustion is introduced through the double casing around the burners. The concentrated red liquor is atomized, into the furnace, at 60 to 65 pounds per square inch and 235° F. through the stationary nozzles. The actual combustion chamber or fire box is approximately 13 feet wide by 14 feet deep by 18 feet high. The concentrated sulfite liquor is burned under self-sustaining combustion conditions with furnace temperature and gas velocity producing a dry magnesium oxide ash of high purity and reactivity. Separation of the magnesium oxide ash from the furnace gases is accomplished by the use of multiclone separators (8E) located after the air heater and preceding the cascade evaporators (Figure 2). The multiclones are equipped with star valves at the bottom discharge permitting operation against the induced draft. The magnesium oxide ash is conveyed by a screw conveyor to a slurry tank where make-up magnesium oxide is added and the slurry pumped to the sulfur dioxide absorption towers. The furnace gases from which the ash was removed go to the cascade evaporators previously described and then to cooling towers before passing finally to the sulfur dioxide absorption towers.

The boiler plant produces steam for two 6250-kv.a. turbo-generators in an adjoining room where power for operating both the sulfite and sulfate mills is generated (Figure 3). The generators (5E) operate on steam at 725° F. and 615 pounds per square inch. The turbines exhaust at 35 pounds per square inch and bleed at 135 pounds per square inch. The power plant is fully and automatically controlled from a central control board. Power distribution is shown in Figure 3.

In pilot plant operations and the first installation at Longview, mechanically driven integral fan oil burners were used. However, considerable difficulty was experienced with baking of organic solids on the inner cup of the burner under continuous operating conditions. The steam atomizing burners were installed to overcome this difficulty, and since then it has been possible to operate the units at expected capacity with the production of reactive ash of very good quality. Some difficulty has been encountered with fouling of boiler passes or tube surfaces, and hand lancing is sometimes necessary to keep the furnaces relatively clean and in condition for continuous operation. To facilitate cleaning, automatic soot blowers have been installed.

Acid Making

To complete the cyclic process, the cooking liquor, as it is used in digesting the wood chips, must be prepared from the recovered chemicals. This part of the process is shown in Figure 2.

The sulfur dioxide gas from the furnaces at 300° F. is cooled to 120° F. in two all-steel cooling towers lined with acid-resisting brick and filled with 4- and 6-inch ceramic partition tile. The towers are 16 feet in diameter and 50 feet high. The circulating cooling water containing some sulfur dioxide is cooled from 160° to 110° F. with twelve sections of water-cooled heat exchangers and then returned to the top of the gas cooling tower. The cooled sulfur dioxide gas is then absorbed in six concrete absorption towers in two series of three each following each of the two recovery units. The towers are 16 feet in diameter and 50 feet high, have a 3-inch acid-resisting tile lining, and are packed with 6-inch cross partition ceramic tile supported by carbon uprights and beams. The towers are necessarily large since the concentration of sulfur dioxide is of the order of 1% or less, and the quantity to be absorbed is approximately 360 to 400 pounds of sulfur dioxide per ton of pulp produced.

A 10% magnesium hydroxide slurry, from the magnesium oxide slurry tank, is fed at the rate of 20 gallons per minute to the top

of the tower (in which the furnace gas first enters) at 15 gallons per minute to the second tower and at 5 gallons per minute to the third. These quantities are approximate but represent the full amount of magnesium hydroxide slurry going to the towers from both recovered and added magnesium oxide. The absorbing liquor is circulated at about 1000 gallons per minute from the bottom of each tower back to the top of that same tower by vertical type pumps operated by 50-hp., 1200-r.p.m. synchronous motors. Most of the make-up water is added to the last tower.

Theoretically, a sufficient quantity of sulfur dioxide would be available from the burning of the strong red liquor to react with the recovered and added magnesium oxide to form magnesium bisulfite with little or none of the monosulfite salt. Actually, the magnesium sulfite is in the range 0 to 0.3% and is controlled by regulating the quantity of make-up sulfur dioxide introduced into these towers. Under the existing conditions (pH of 4 to 5) calcium salts are in their most insoluble state and the calcium picked up from original wood and make-up magnesia is removed by a sand filter.

The raw acid is then fortified in two absorption towers with sulfur dioxide produced from sulfur in a small rotary burner. One tower is constructed of concrete with tile lining and operated at atmospheric pressure; the second, which is operated at a pressure of 15 pounds per square inch, is of steel construction, lined with acid-resisting tile, and packed with ceramic partition tile.

Materials of Construction

The corrosive nature of the acid cooking liquor requires stainless steel in all equipment where contact with metal occurs. Type 316 stainless steel is used in all tubing and pipes that convey the liquor throughout the cooking and recovery plants. Type 316 is also used in all pumps and processing equipment where metal contact is made. Acid-resisting brick and tile are used as linings for digesters, dump tanks, and absorption and acid-fortifying towers, which are constructed of steel plate and/or concrete. Litharge and glycerol or an acid resin jointing is used in cementing of linings. Wood stave tanks are used at the points indicated.

Over-all Operation and Recovery

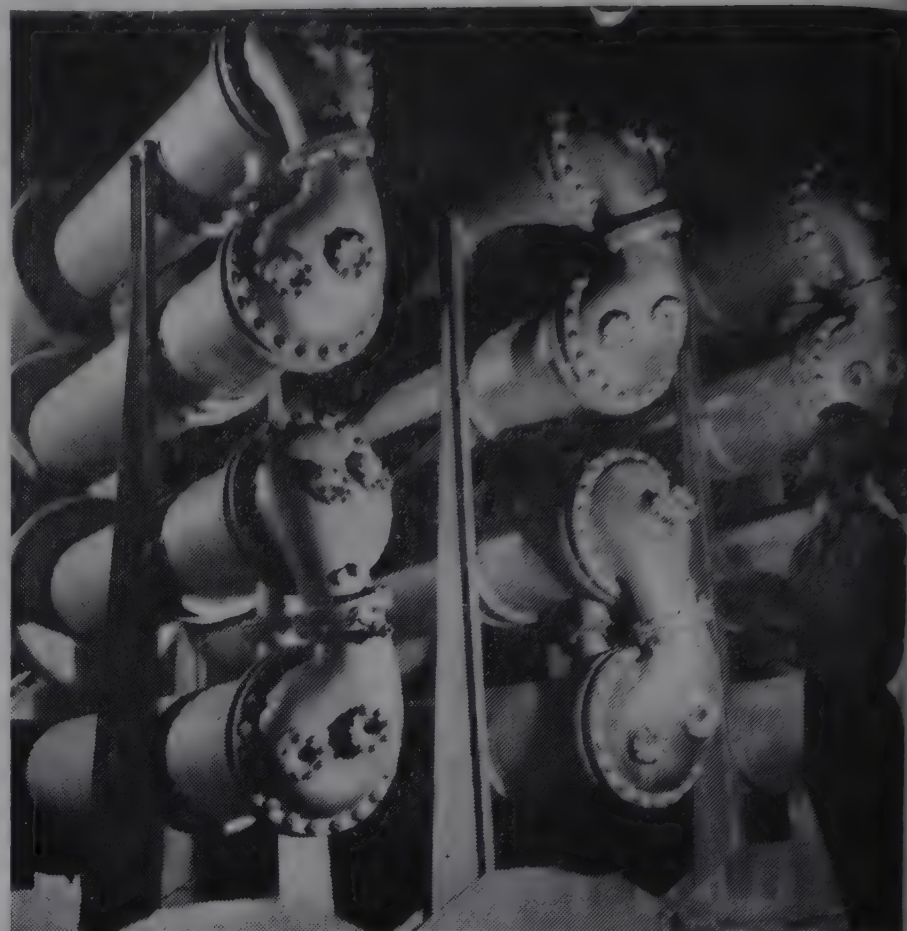
In the operation of the Longview mill to the present time, chemical consumption has been abnormally high and steam generation below that expected owing to the lack of sufficient evaporator capacity to evaporate all the red liquor available. The mill is currently producing 300 to 325 tons of unbleached pulp per day, whereas the recovery system was designed for a 275-ton-per-day output.

Most representative figures for operations over appreciable periods of time show the magnesium oxide consumption to be 50 pounds per ton of pulp produced. Sulfur consumption, also higher than was anticipated, is 85 pounds per ton of pulp.

With sufficient evaporator capacity, which is presently being installed, the magnesium oxide consumption is expected to drop to 20 pounds and sulfur consumption to 50 pounds; steam generation is expected to increase to 9000 pounds of steam at 615 pounds per square inch and 725° F. per ton of pulp. A future report will describe recovery after these changes are complete and operating data have been accumulated. Calcium-base pulping requires 270 pounds of sulfur and 350 pounds of lime rock per ton.

FUTURE PROSPECTS

Magnesium oxide pulping, though not yet developed to a state of perfection, is definitely a solution to the sulfite pulp making stream pollution problem. The process is one which fully utilizes the energy content of the organic waste and recovers the chemicals used in cooking; all products recovered are immediately used by the pulp industry. Until such time as markets develop for products that can be recovered from waste liquor solids by other



Heat Exchangers on Sulfur Dioxide Gas Cooling Towers

processes and that are economically of greater value than their use as a fuel, the magnesium oxide process offers sound utilization of sulfite waste liquors and elimination of stream pollution. The increased evaporator capacity now being installed at Longview, Wash., is expected to result in greater recovery of cooking chemicals and will further enhance the economics of the process.

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- (3E) Electric Steel Foundry Co., Portland 10, Ore., special single-pass heaters.
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- (5E) General Electric Co., Schenectady, N. Y., 6250-kv.a. turbo-generators.
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Kraft Pulp Production



Kraft Pulp Coming Off Vacuum Washers at Camas, Wash., Mill of Crown Zellerbach Corporation

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in collaboration with

**WALTER F. HOLZER AND
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Crown Zellerbach Corporation, Camas, Wash.

A NATION'S standard of living roughly parallels its consumption of pulp and paper. Each day every person in the United States uses almost 1 pound of paper (9), which is much more than is used in any other country. With yearly production about 30% that of steel by weight (1, 10), the size of the industry is impressive. Even more impressive is the important role played by chemistry and chemical engineering in making pulp and paper.

It all began several thousand years ago when glued strips of papyrus replaced cumbersome clay tablets as writing mediums. The Chinese later made paper from a mixture of bamboo fiber and old rags.

Chemistry actually entered the process only when wood became the cellulosic raw material. The problem was twofold: to remove most of the lignin binding the cellulose fibers in wood; and to retain the fibers with a minimum of degradation. At present this is accomplished in three chemical processes—soda, sulfite, and kraft (sulfate). The soda process uses sodium hydroxide to dissolve noncellulosic materials from the wood. The sulfite process attains similar ends with an acid cooking liquor. A

mixture of sodium hydroxide and sodium sulfide is used to make kraft pulp (Table I).

During the latter part of the nineteenth century, much salt cake (sodium sulfate) was available as a by-product from the manufacture of hydrochloric acid. The German chemist, Dahl, found a new use for this salt cake when he invented the kraft process in 1889. Kraft means "strong" in German, an apt description of that kind of pulp or paper. Small quantities of it were made in Germany and Sweden before 1900. The first kraft mill in North America was located in East Angus, Quebec, in 1908.

The process developed rapidly, especially in areas where large quantities of pine were available. This wood is not commonly pulped by the sulfite treatment because the heartwood contains pinosylvins (3,5-dioxystilbene) and its monomethyl ether which prevent digestion of the wood by acid liquor (2). Pine is readily pulped by alkaline kraft liquor. Large stands of Southern pine in Alabama, Arkansas, Louisiana, Georgia, and Florida became the raw material for growth of a large kraft industry in those states.

Another great timber area of the United States is the Pacific Northwest. Until recently, large stands of Douglas fir were untapped for pulp because the wood resists sulfite pulping. This is due to low permeability and the presence of certain phenols—for example, taxifolin, a flavanone—which form insoluble lignin compounds (7).

It was not until World War II that Douglas fir was pulped by the kraft process in regular and substantial quantities. This represented culmination of plans begun in 1925 when the Crown Zellerbach Corporation built a kraft mill at Camas, Wash., on the Columbia River. At present this mill is one of the nation's largest in total production with its daily capacity of 360 tons of kraft pulp (averaging 38% Douglas fir, with as much as 65% in some grades), 350 tons of sulfite pulp, and 30 to 35 tons of groundwood.

In general, kraft pulp goes into wrapping and bag paper, shipping cases, and other papers where high strength must be combined with low cost. Four hundred different papers are made at Camas, Wash., although the accent is on lightweight tissue grades. This mill is the largest unit of seven pulp and paper mills comprising the parent Crown Zellerbach Corporation. Others

TABLE I. PROCESS AND PRODUCT CHARACTERISTICS

	Kraft	Sulfite	Soda
Cellulosic raw material	Almost any kind of wood, hard and soft; Camas uses hemlock, Douglas fir, and white fir; woods cooked separately but all blown into same tank	Wood should be of good color and must be free of certain hydroxy phenolic compounds such as pinosylvins in pine (7) and flavanone in Douglas fir (11); Camas uses hemlock and white fir	Any wood that can be used in kraft; low yields and strength of this pulp limit its production to short-fibered hardwood pulps which are used as filler in book and magazine grades
Cooking liquor composition	A 12.5% solution of NaOH, Na ₂ S, and Na ₂ CO ₃ ; typical analysis of solids: 58.6% NaOH, 27.1% Na ₂ S, 14.3% Na ₂ CO ₃ ; dissolving action due to first two; carbonate is inactive and represents the equilibrium residue between lime and Na ₂ CO ₃ in the formation of NaOH	7% by weight SO ₂ , of which 4.5% is combined as sulfurous acid and 2.5% as calcium bisulfite; cooking one ton of pulp requires 225 to 300 pounds of sulfur and 350 to 400 pounds of lime rock	12.5% solution of NaOH and Na ₂ CO ₃ in the ratio 85:15; dissolving action due solely to NaOH
Cooking conditions	Time: 2–5 hours; temperature: 340–355° F.; pressure: 100–125 lb./sq. in.	Time: 7–12 hours; temperature: 265–300° F.; pressure: 70–90 lb./sq. in.	Time: 6–8 hours; temperature: 330–340° F.; pressure 90–105 lb./sq. in.
Chemical recovery	Chemicals too expensive to discard; therefore, most of process is devoted to recovery of cooking chemicals with incidental recovery of heat through burning liquor organic matter dissolved from wood; chemical losses from system are replenished with salt cake, Na ₂ SO ₄	SO ₂ relief gas recovered; liquor discarded after wood digestion and pulp washing; no present salvage of chemicals but use of waste liquor being extensively studied	Sodium hydroxide recovered and re-used as in kraft process, but make-up chemical is Na ₂ CO ₃ instead of Na ₂ SO ₄
Materials of construction	Digesters, pipe lines, pumps, and tanks can be made of mild steel or iron because caustic liquor does not readily corrode them; however, for more severe service Camas uses stainless steels such as Types 430 and 304	Acid liquor requires digester lining of acidproof brick; fittings of chrome-nickel steels (Type 316), lead, and bronze	Same as kraft materials
Pulp characteristics	Brown color; difficult to bleach; strong fibers; resistant to mechanical refining	Dull white color; easily bleached; fibers weaker than kraft	Brown color; easily bleached; fibers weaker than kraft or sulfite
Typical paper products	Strong brown bag and wrapping; multiwall bags, gumming paper, building paper; strong white papers from bleached kraft, paper boards such as used for cartons, containers, milk bottles, and corrugated	White grades: book paper, bread wrap, fruit tissue, sanitary tissue	Usually blended with other pulps; book and magazine grades, coated papers, sanitary tissue

are located in West Linn, Ore., Lebanon, Ore., Port Townsend, Wash., Port Angeles, Wash., Ocean Falls, B. C., and Carthage, N. Y.

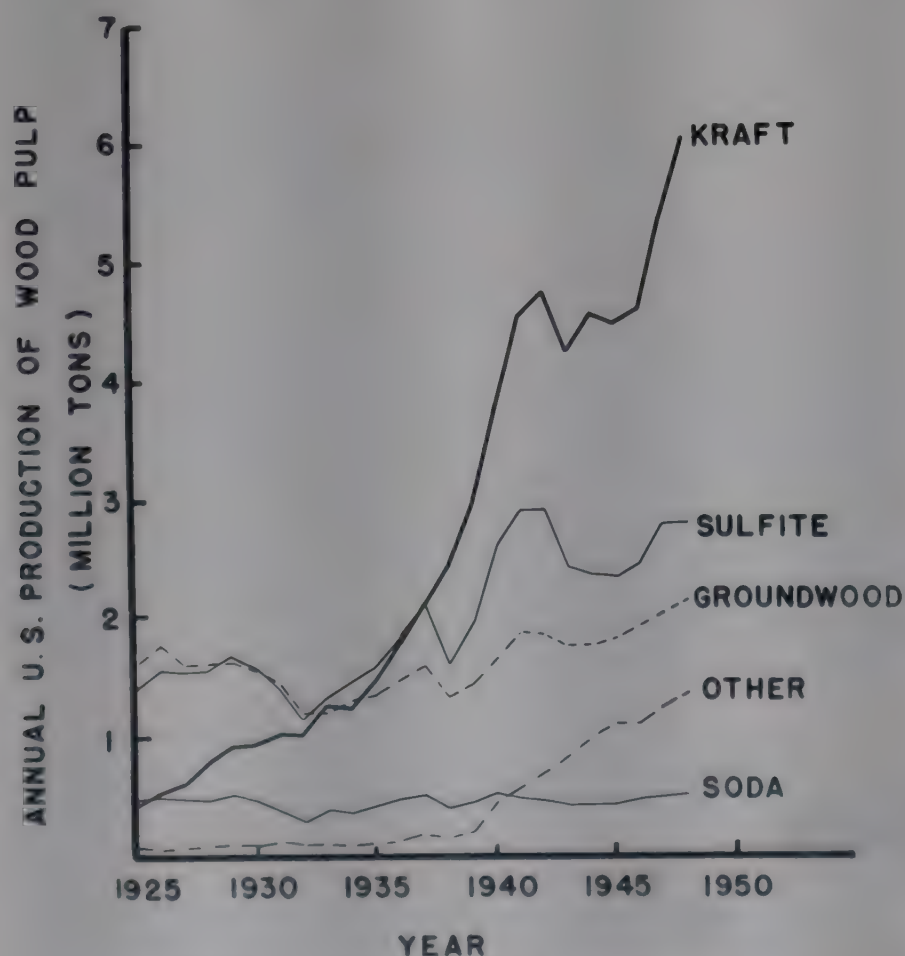


Figure 1. Domestic Pulp Production (11)

THE CAMAS MILL

The phenomenal growth of the kraft industry (Figure 1) can be appreciated when it is realized that the Camas mill of the Crown Willamette Paper Company (a division of Crown Zellerbach Corporation) produces ten times the entire kraft pulp output of the United States and Canada of 40 years ago. The present size of the industry by geographical areas is shown in Table II.

The Camas plant uses about 600,000 board feet (1200 cords) of pulpwood a day. To feed this voracious appetite and that of the

TABLE II. 1948 U. S. KRAFT PULP PRODUCTION BY REGIONS (12)

	Pulp (Air-Dry Weight) ^a , Tons				
	New England and Middle Atlantic	Lake	Pacific	South	Total
Bleached	84,227	49,449	82,959	822,053	1,038,688
Semibleached	0	43,769	36,872	148,700	229,341
Unbleached	93,785	219,934	377,698	4,065,776	4,757,193
Total	178,012	313,152	497,529	5,036,529	6,025,222

^a As reported to U. S. Pulp Producers Association by 98% of industry and estimated for 2%.

other Crown Zellerbach mills, the company practices a program of sustained yield logging on 200,000 acres of forest land in Washington and 300,000 acres in Oregon. A small amount of additional wood must be bought to satisfy the total needs. The forest lands are located in several distinct areas. The rain forests of the Pacific Coast contain mostly western hemlock and Sitka spruce. On the west slope of the Cascade Mountains south and east of Oregon City, Ore., the predominant species is Douglas fir. Both sides of the Columbia River have large stands of Douglas fir. The Olympic Peninsula grows mainly western hemlock.

These areas are being developed on a long-term basis. Roads through the forests are of the permanent type and are strategically located to allow access for fire protection. They enable loggers to get to any area for harvesting logs according to the plan best suited to that particular area. This may mean selective cutting by thinning or by clearing small blocks. Cutover land is being brought back to production by hand planting of seedlings and by helicopter broadcast of seeds. Although the latter is far cheaper, its use for only 3 years would make any statement on its success premature.

Forest rodents were found to eat large quantities of the tree seeds soon after their aerial distribution. It has been found necessary to do extensive poisoning prior to seeding. An area of poisoned grain several hundred yards wide surrounds the area to be seeded. Then the seeds are distributed. By the time the rodents have eaten their way through the poison barrier, the trees have sprouted and are safe from attack.

Using an average figure of 2 cords of wood (1000 board feet) per acre per year as the production of the land, it requires about 200,000 acres of forest to sustain the Camas mill. This does not allow for any natural catastrophe, insect damage, or fire. A 60-year growing cycle is calculated for pulpwood logs; sawmills use a 100-year cycle.

More than half of the logs for pulpwood are cut in the field by gasoline or electric chain saws. The logs are from 30 to 60 feet long and up to 6 feet in diameter, averaging 1 to 2 feet. The logs are trucked to the nearest navigable water. Most of the wood for Camas is dumped into the Columbia River near its mouth. Some comes via the Willamette River. The logs are made into a flat raft containing about 200,000 board feet. Butt logs of hemlock are waterlogged on the stump. For floating to the mill, they are mixed with buoyant top hemlock logs and then gathered in round bundles tied with iron hoops. The flat and round rafts are floated to storage waters capable of holding several months' supply for the mill.

Two large jaw cranes lift the logs out of the river. The logs are cut to standard 24-foot lengths and carried by cross conveyor to a hydraulic barker (13E). Geared wheels rotate the logs up to 40 r.p.m. under a perpendicular jet of high pressure water (1400 pounds per square inch, 1200 gallons per minute). One lengthwise pass of the jet is sufficient to erode off all the bark. The barker capacity is four to eight logs per minute, depending on diameter.

A more common and older method for removing bark is by means of a cylindrical drum made of iron angles. Logs (cut 2- to 4-foot lengths) enter continuously at one end and the rotation of the drum on the long axis tumbles them against each other and against the inside of the drum, wearing off the bark. After a retention time of 0.5 to 2 hours, the logs are continuously forced out the other end. Besides the bark, 5 to 6% useful wood, which represents waste, may be ground off. The hydraulic barker is displacing the drum counterpart in many mills.

From the hydraulic barker at Camas, the bark is sent to a waste heat furnace and the clean logs are conveyed to a chipper (14E). This is a 153-inch diameter heavy steel disk set with six knives and rotated at 257 r.p.m. by a direct-connected 1500-hp., 7000-volt synchronous motor. Logs up to 34 inches in diameter can be chipped. If the machine were supplied with a

continuous stream of 30-inch diameter logs, it could convert to chips over 200,000 board feet of logs (400 cords) each hour. The Camas maximum daily requirement is about 650,000 feet board measure (1300 cords). After moving down a short chute, the logs press against the whirling chipper blades and are completely converted to chips. Screen analyses are taken daily and hand measurements weekly. Typical monthly average chip analyses by screening and hand measurement are shown in Table III.

TABLE III. SIZE OF WOOD CHIPS

Screen Analysis		Hand Measurement	
Screen size, inch	Retained, % of weight	Length, inches	% by weight
		Trash	0.5
1	1.8	1 inch and over	3.0
3/4	18.4	7/8	9.5
1/2	46.4	3/4	34.2
1/4	30.2	5/8	38.0
1/8	2.2	1/2	10.5
Through 1/8	1.0	3/8	2.7
		1/4	1.0
		Less than 1/4	0.6

The chips are screened (1E), and those over 1 inch long are sent back to a chip breaker; after this they are returned to the system. Anything under 0.25 inch long is considered dust and is sent to the steam plant. Those chips that are not going to be used immediately for pulp are conveyed to one of four storage silos. This permits segregation of four species or grades of wood.

The complex details of the kraft process can be better understood with the help of the following résumé: Wood chips are digested or cooked with an alkaline liquor. The active cooking chemicals (sodium hydroxide and sodium sulfide) dissolve the cementing lignin material of the wood. The liberated fibers (largely cellulose) and spent chemicals are separated on vacuum washers. At this point the fibers are ready for screening and subsequent papermaking.

The remainder of the process is concerned with recovery of the chemicals. Multiple-effect and disk evaporators remove water from the weak liquor until it is sufficiently concentrated to burn. In the recovery furnace, burning accomplishes separation of organic from inorganic chemicals by destroying the former; conversion of inorganic chemicals to sodium carbonate and sodium sulfide; and production of heat and power. All heat requirements of the kraft mill are supplied by the recovery furnace. The molten inorganic chemicals from the furnace are dissolved in water to form "green" liquor, which after clarification is treated with lime to regenerate sodium hydroxide. This liquor with its active constituents (NaOH and Na₂S) is "white" liquor which is then used for digestion of wood at the beginning of the pulping process. The lime spent in causticizing is washed, burned, and recycled.

STATIONARY DIGESTERS

The large cooking vessels known as digesters are generally stationary, but a few mills such as Camas use the tumbling or rotary type. Since the former is more commonly used in kraft pulping, it will be described first.

The stationary digesters of the Port Townsend, Wash., mill of Crown Zellerbach are typical of the industry. They are cylinders with a volume of 2500 cubic feet and are fitted with a bell top and cone bottom. They are built of 1³/₁₆-inch steel plate with over-all height of 35 feet and diameter of 10.5 feet. The rated capacity of each cook is 6.5 tons of pulp on an air-dry basis (10% moisture). Each digester is equipped with an external stainless steel two-pass tube heater (steam on outside) with a heating surface of 485 square feet.

Chips are run into the digester by gravity from overhead bins. The flow of chips is maintained by steam jets located near the bin bottoms; at the same time the cooking and diluting liquors are



Digester Blow Tanks, Cyclone Separator, and Pipe Line to Steam Heat Recovery

run into the top of the digester. The force of the streams packs the chips, thereby increasing the digester charge by about 10%.

The cooking liquor is circulated through the heater and digester by an 1800-gallon-per-minute centrifugal pump driven directly by a 50-hp. 870-r.p.m. motor. Liquor is pulled through a strainer one third of the way up the digester, forced through the heater, and returned to the digester in split flow—about one third to the bottom and two thirds to the top.

The active cooking chemicals are contained in the "white" liquor (see Figure 5 for analysis) and amount to 15.5% on the dry weight of wood, with all chemicals expressed as Na_2O . A typical charge to a stationary digester comprises 760 cubic feet of white liquor, 525 cubic feet of black liquor, and 23.3 tons of wood chips (12.3 tons air-dry basis).

White Liquor Composition

	Lb. $\text{Na}_2\text{O}/\text{Cu. Ft.}$
Total alkali	6.68
Active alkali	5.78
Sulfide	1.52
Sulfate	0.23
Sulfite	0.11
Chloride	0.37

Sodium carbonate is inactive in the cooking process. A white liquor high in sodium sulfide is a very important factor in producing pulp of high strength and quality. A low sodium sulfide liquor resembles in cooking action that of the soda process which makes a low strength pulp. The less drastic dissolving action of

kraft cooking liquor accounts for its 10% greater pulp yield than in the soda process.

The role of sodium sulfide in kraft pulping is explained (3) as follows: Lignin of wood reacts in the solid phase with sulfide ion. This appears to facilitate the subsequent cleavage of lignin from the fiber. The sulfur blocks active groups of the lignin, thereby preventing condensation to large insoluble molecules. The cooking liquor then dissolves the lignin which has been rendered more soluble by its reaction with sulfur.

In the stationary digester enough black liquor (Figure 5) (comprising 40 to 45% of total liquor volume) along with white is added to cover the chips. Black liquor is used instead of water for volume make-up in order to eliminate dilution of liquor which would increase the load on the evaporators and subsequent recovery.

The cook is brought to 344° F. and 110 pounds per square inch as rapidly as possible; this requires 2 hours. Temperature is maintained for about 25 minutes with adjustment of the exact time by examination of pulp samples blown from the digester. Pressure is relieved to 80 pounds and the digester blown to a blow tank through a cyclone separator.

In a kraft cook it is important that air in the digester and in the pores of the chips be relieved as early as possible because oxygen has a powerful degrading action on cellulosic materials in the presence of hot alkali. Air removal is accomplished by venting the top of the digester to the atmosphere. The end point of the relief is reached when the steam pressure and temperature correspond.

ROTARY DIGESTERS

Wood digestion is accomplished at Camas in ten rotary or tumbling digesters (5E). Each of five units is 9 feet 10 inches in diameter, 26 feet high, has a volume of 1460 cubic feet, and can cook 3.5 tons of pulp (air-dry basis). Each of the remaining five units is 10 feet 3 inches in diameter, 30 feet high, with a volume of 1884 cubic feet, and can cook 4.5 tons of pulp (air-dry basis).

The digester is mounted on trunnions attached to a heavy reinforced central section. This arrangement has been found superior to mounting on a shaft through the shell. Previous digester shells expanded more than the shaft allowed, causing accelerated corrosion in the stressed area.

The digesters are built with a safety factor of 5, based on the tensile strength of the steel. Use of an all-stainless steel shell would be prohibitively expensive; therefore, the necessary structural strength is obtained with 1.25 inches of steel boiler plate. Six units are lined with Type 405 stainless steel, $\frac{7}{16}$ inch thick, and resistance welded. Stainless steel linings being tried by other pulp manufacturers include Types 304, 316, and 347. The four unlined digesters are made of high silicon steel because it is cheaper and more corrosion resistant than ordinary boiler plate.

Alloy linings are used for several reasons. They have longer life against the gradual corrosion of the alkaline liquor. More frequent replacement of ordinary steel digesters is expensive from a material as well as labor standpoint. The life of an unlined digester made of boiler plate is estimated at 10 years based on a penetration of $\frac{1}{16}$ inch per year. An all-high silicon steel unit can be used for 12 years.

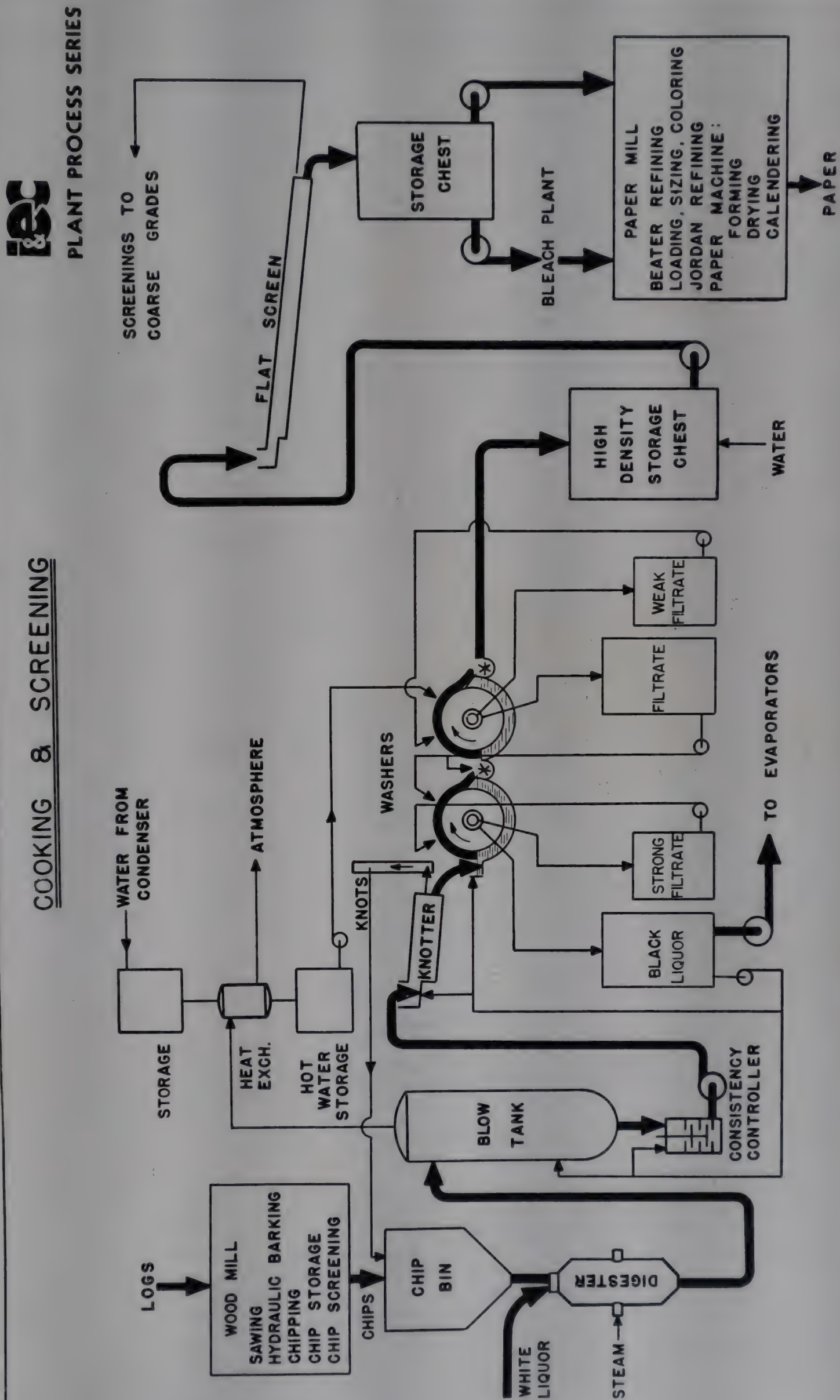


Figure 2. Flow Sheet of Cooking and Screening Processes in Production of Kraft Pulp at Camas, Wash., Mill of Crown Zellerbach Corporation

TABLE IV. SEXTUPLE-EFFECT EVAPORATOR TEST

MATERIAL BALANCE		Lb./Hr.					
Feed of weak black liquor = 2850 cu. ft./hr. \times 1.09 (sp. gr.) \times 62.4 lb./cu. ft.		194,000					
Discharge from evaporator = 194,000 lb./hr. \times $\frac{17.5 (\% \text{ solids in inlet liquor})}{53.3 (\% \text{ solids in discharge liquor})}$		63,700					
Total evaporation of water accomplished in evaporator		130,300					
Lb. H ₂ O evaporated/lb. steam = $\frac{130,300 \text{ lb./hr. (total evaporation)}}{26,000 \text{ lb./hr. (steam consumption)}} = 5.01$							
	Flash Tank	Evaporator Test Effect ^a					
		I	II	III	IV	V	VI
Chest pressure, lb./sq. in. gage	...	36.5	15.0	9.2	-4.0 ^b	-15.0 ^b	-21.2 ^b
Chest temp., ° F.	...	282	249	226	205	179	156
Temp. difference, ° F.	...	21	12	12	14	11	31
Liquor temp. calcd., ° F.	217	261	237	214	191	168	125
Liquor temp. measd., ° F.	206	263	234	210	186	164	129
Boiling point rise	11	11	10	8	7	5	6
Dome temp., ° F.	206	250	227	206	181	163	119
Dome pressure, inches Hg	...	30.8	10.5	-3.5	-13.3	-19.6	-26.7
Latent heat of vaporization B.t.u./lb./° F.	974	946	961	974	990	1000	1026
Total solids, lab., %	53.3		37.9	31.3	25.9	22.4	24.3
Total solids, calcd., %	...	51.4					
Feed, lb./hr.	66,000	90,000	108,500	131,000	145,300	95,300	98,700
Discharge, lb./hr.	63,700	66,000	90,000	108,000	131,000	74,300	71,000
Evaporation, lb./hr.	2,300	24,000	18,500	23,500	14,300	21,000	27,700
Evaporation (heat bal.), lb./hr.	2,240	23,500	21,700	22,100	19,800	22,300	28,500
Over-all temp. difference, %	...	20.8	11.9	11.9	13.8	10.9	30.7
Acceptance test No. 1	...	30.8	7.5	9.4	15.0	15.0	22.4

HEAT BALANCE

	Q (Heat Requirement), M B.t.u./Hr.	Latent Heat of Vaporization, B.t.u./lb./° F.	Lb. H ₂ O Evaporated	Effect
Liquor flash ^c (66,000) (261-217) (0.75)	2,180	974	2,240	Flash tank
Steam feed (26,000) (923)	24,000			
Heat liquor to I (90,000) (261-237) (0.83)	-1,790			
B.t.u. to II from evaporation of liquor	22,210	946	23,500	
Steam condensate flash (26,000) (282-249)	860	946	910	
Total B.t.u. to II	23,070		24,410	
Heat liquor to II (108,500) (237-214) (0.87)	-2,170			
B.t.u. to III from evaporation of liquor	20,900	961	21,700	II
Steam condensate flash (26,000-910) (249-226)	580	961	600	
Condensate flash (24,410) (249-226)	560			
Liquor flash	2,180	974	2,240	
Total B.t.u. to III	24,220		24,540	
Heat liquor to III (131,000) (214-191) (0.89)	-2,680			
B.t.u. to IV from evaporation of liquor	21,540	974	22,100	III
Condensate flash (24,410 + 24,540) (226-205)	1,030			
Total B.t.u. to IV	22,570			
Heat liquor to IV (145,300) (191-168) (0.90)	-3,010			
B.t.u. to V from evaporation of liquor	19,560	990	19,800	IV
Condensate flash (24,410 + 24,540 + 22,100) (205-179)	1,850			
Total B.t.u. to V	21,410			
Cool liquor to V (95,300) (168-178) (0.92)	880			
B.t.u. to VI from evaporation of liquor	22,290	1000	22,300	V
Condensate flash (24,410 + 24,540 + 22,100 + 19,800) (179-156)	2,090			
Total B.t.u. to VI	24,380			
Cool liquor to VI (98,700) (125-178) (0.92)	4,810			
B.t.u. to condenser from evaporation of liquor	29,190	1026	28,500	VI
Total for the 6 effects	139,650,000		140,100	

Six-unit over-all head coefficient: $U = \frac{Q}{A \Delta t}$ $A = 4433 \text{ sq. ft. av.}$ $U = \frac{139,650,000}{4433 \times 101} = 315$

^a Total temperature difference in 6 effects = 101° F.; inlet weak black liquor temperature = 178° F.; barometric pressure on 9/29/49 = 30.05 inches Hg.

^b Inches of mercury.

^c (Lb./hr. feed) (temp. diff.) (spec. heat, B.t.u./lb.).

In recent years, alloy steels have become cheaper and the methods of fabrication have improved greatly. Welding can be done in the field instead of in the shop. Stainless steel is available as either resistance-welded or rolled onto the steel shell. This applies not only to the digester but wherever alloys are justified. All of the digesters are insulated with 1.25 inches of magnesia blocks cemented with a waterproof mastic emulsion protective covering.

A digester is charged by rotating it to the vertical position, then filling with wood chips from an overhead bin (Figure 2). The cooking liquor is run in at the same time from a calibrated tank. Charge to the five smaller units comprises 23,500 pounds

of cooking liquor and 26,000 pounds of wood (50% moisture). Charge to the five larger units comprises 30,000 pounds of cooking liquor and 33,500 pounds of wood (50% moisture).

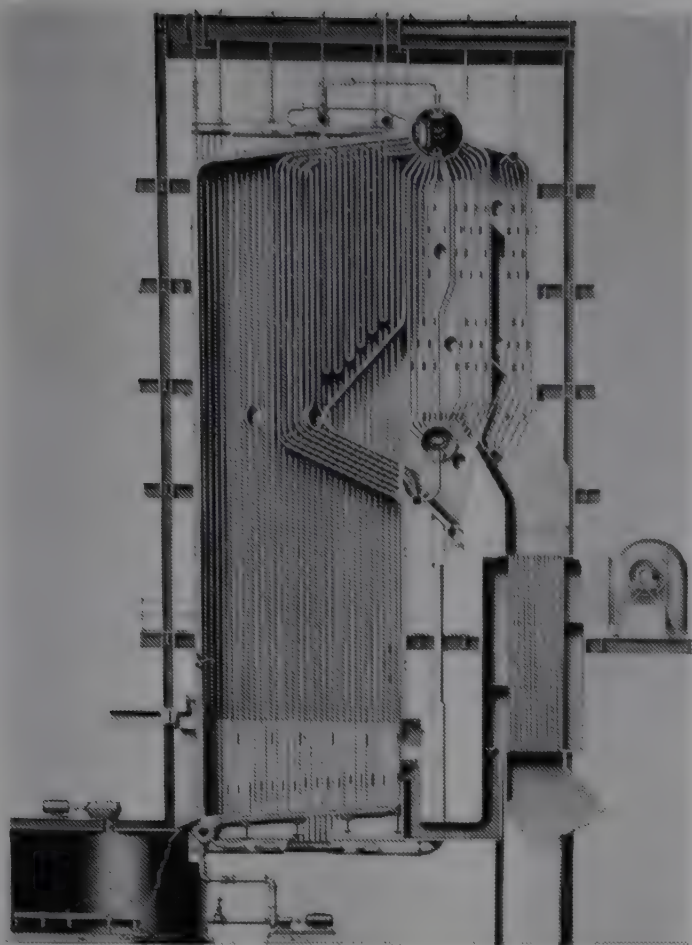
The digester is rotated at 0.2 r.p.m., and the wood is cooked with direct steam at a pressure of 110 pounds per square inch (340° F.). The steam input is automatically cam-controlled by means of a time-pressure template (10E). Heat-up requires 1.25 hours; then the charge is held at 340° F. for an additional 0.75 hour, after which the pressure is relieved to 80 pounds per square inch, then sampled and blown. The sample is usually taken one or two rotations before the pulp is expected to be completely cooked to permit any necessary changes in cooking time.

The pulp is blown tangentially into the top of the blow tank. Steam is exhausted from the top to a heat exchanger (1760 tubes, 16 feet long, 1 inch outside diameter). The heat given up to process water outside the tubes is the sensible heat from 340° down to 212° F. plus the latent heat of condensation (17E). Meanwhile, the pulp and black liquor (Figure 5) drop to the bottom of the blow tank. For each ton of pulp, the associated black liquor contains 3000 pounds of solids, of which 1300 pounds are recoverable chemicals. The remainder comprise the organic solids from the wood.

The blow tank is 40 feet high, 14 feet in diameter, and made of 3/8-inch mild steel plates. An agitator on a vertical shaft extends through the bottom to mix the stock with additional black liquor. This is spent liquor formed in previous digestions and

separated from the pulp at the washers. Dilution is necessary to obtain sufficiently low consistency for pumping. The stock in the blow tank and consistency regulator is diluted from 15 to 2.5% solids.

The consistency regulator is a steel tank 8 feet high and 4 feet in diameter fitted with blades pitched slightly upward. A central shaft, turned by a 2-hp. motor, is also fitted with blades. As the pulp consistency increases, the load on the motor increases, as measured by a potentiometer, and an air-actuated device opens vents to admit more black liquor to dilute the stock. When this happens, the load on the motor which drives the paddles is decreased to a point where the black liquor flow will be



Two-Drum-Type Black Liquor Recovery Furnace

throttled. Consistency must be controlled within narrow limits in order to form a uniform mat of optimum thickness on the following washers.

A 40-hp. variable-speed motor drives a centrifugal pump running 800 to 900 r.p.m. (maximum speed 1200 r.p.m.) which sends the pulp to knotters (3E) for removal of knots and oversized chips. Knotters are a series of flat vibrating screens with $\frac{3}{8}$ -inch round openings. Stainless steel screens are now used after it was found that for some unknown reason mild steel screens clogged more readily, causing poor separation of sizes. The rejects are conveyed back to be mixed with chips entering the digesters, where a second cook will defiber the knots and oversize chips. Pulp which passes through the holes goes by gravity to the washers.

It is necessary to wash the maximum amount of chemical from the pulp with a minimum amount of water, hence multiple-stage washing. This is accomplished in two 2-stage rotary vacuum washers in series so that in effect the washing is 4-stage (16E). The effluent is pumped and showered on the pulp mat countercurrent to the pulp flow. Between the first and second washer or between the second and third stages there is an inter-pulper which is a small tank with agitator. Effluent from the third stage dilutes the pulp to 1% or less consistency; it then goes to the second washer or the third stage of the system to form a mat. The pulp coming off the washers is 17% consistency. Hot water at 150° F. is added to the mat only on the last stage. The capacity of the washers is about 1.2 tons of pulp per square foot of wire surface per 24 hours. Vacuum on the wire is 8 to 10 inches of mercury. The pulp at this point leaves the pulp mill for the screen room where it is screened and further treated for bleaching and the paper machine (Figure 2).

EVAPORATION

The function of the evaporators is to remove water, or concentrate the weak black liquor (Figure 3) from the washers to such a density that when it is sprayed into the recovery furnace it will ignite and burn because of the organic matter content. At Camas this concentration is done in two types of evaporators: multiple effect steam evaporators and direct heat or disk evaporators using hot gases from the furnace (Figure 3).

Sextuple-effect vertical-tube rising film evaporators (15E) have been found most effective for concentrating the liquid from

about 15 to 18% to 48 to 54% solids. One pound of steam evaporates 4.7 pounds of water in this evaporator but sometimes greater economy is obtained (Table IV). It is common practice to use stainless steel—for example, type 430—in the first effect because of the corrosive nature of the alkaline liquor at elevated temperatures. The vapor head also has an alloy protection (coating welded to the steel shell). Each evaporator contains 552 2-inch outside diameter tubes, 24 feet long. After the first effect, the tubes in all other effects are ordinary steel. The diameter of each steam chest is 4 feet and dome diameter is 8 feet. The evaporator has an over-all height of 35 feet and the shell is 0.5-inch steel plate. The surface condenser for the evaporator system contains 1146 tubes, 13 feet long and 1 inch outside diameter. Vacuum is obtained by twin-steam ejectors sometimes used in series. In the operation of the sextuple effect evaporators the weak liquor is fed directly into effects V and VI in equal parts. The vapor flash from effect I enters the dome of effect IV.

Because this is one of the few places in industry where sextuple-effect evaporation is regularly carried out, Table IV has been prepared to show material and heat balances taken on September 29, 1949. In comparison with the first acceptance test made by the manufacturer, this test showed a higher evaporation per pound of steam and a slightly lower over-all sum of temperature differences between vapor side and liquor side. This indicated that the tube surfaces, inside and out, were in good condition and that this type of evaporator was well designed for its required service.

Evaporation is carried out in the sextuple-effect evaporator until just before the liquor becomes too viscous to move freely through the tubes without forced circulation. Further concentration is done in two disk evaporators. This type takes advantage of heat that otherwise would be wasted out the stack. The heating gas used to concentrate the liquor comes directly from the waste heat boiler of the spray-type recovery furnace after heat has been removed by an economizer (to heat boiler feed water) and an air preheater (for forced draft).

Each of the two disk evaporators is 8.5 feet in diameter and contains a shaft 8 feet long with 33 disks set on $2\frac{5}{8}$ -inch centers. A motor drives the shaft at 4 r.p.m., causing the disks to rotate in the pool of liquor at the bottom. The liquor sticks to the disks and the hot furnace gases pass over them evaporating some of the water: inlet liquor concentration, 48 to 54% total solids; outlet, 58 to 62%; inlet gas temperature, 380° F.; outlet, 325° F. After leaving the disk evaporator, the liquor is pumped to storage where it is maintained at 190° to 212° F. by circulating through a tubular heat exchanger countercurrent to steam.

From storage, the strong black liquor is pumped to a mixing tank where dust collected from the Cottrell precipitators is added. Then the liquor is pumped to another mixing tank where salt cake (Na_2SO_4) and sulfur are added continuously by means of an automatic weighing device that can be set to a predetermined feed rate depending on the amount of liquor being burned. The salt cake is the make-up chemical for all the soda losses in the process. Sulfur is used to control the sodium sulfide content of the cooking liquor.

The liquor from the second mixing tank is pumped through a heater in which steam is injected directly to increase the liquor temperature to 220° F. It is then sprayed into the recovery furnace.

RECOVERY FURNACE

The spray-type recovery furnace (4E) has displaced the old type rotary furnaces (5). It is rectangular in design and the walls are built entirely of water tubes with plastic chrome refractory cement between them. The water walls on all four sides of the furnace are connected into mud drums at the bottom and into headers at the top which are so connected to the boiler drums that boiler water is circulated continuously through the walls.

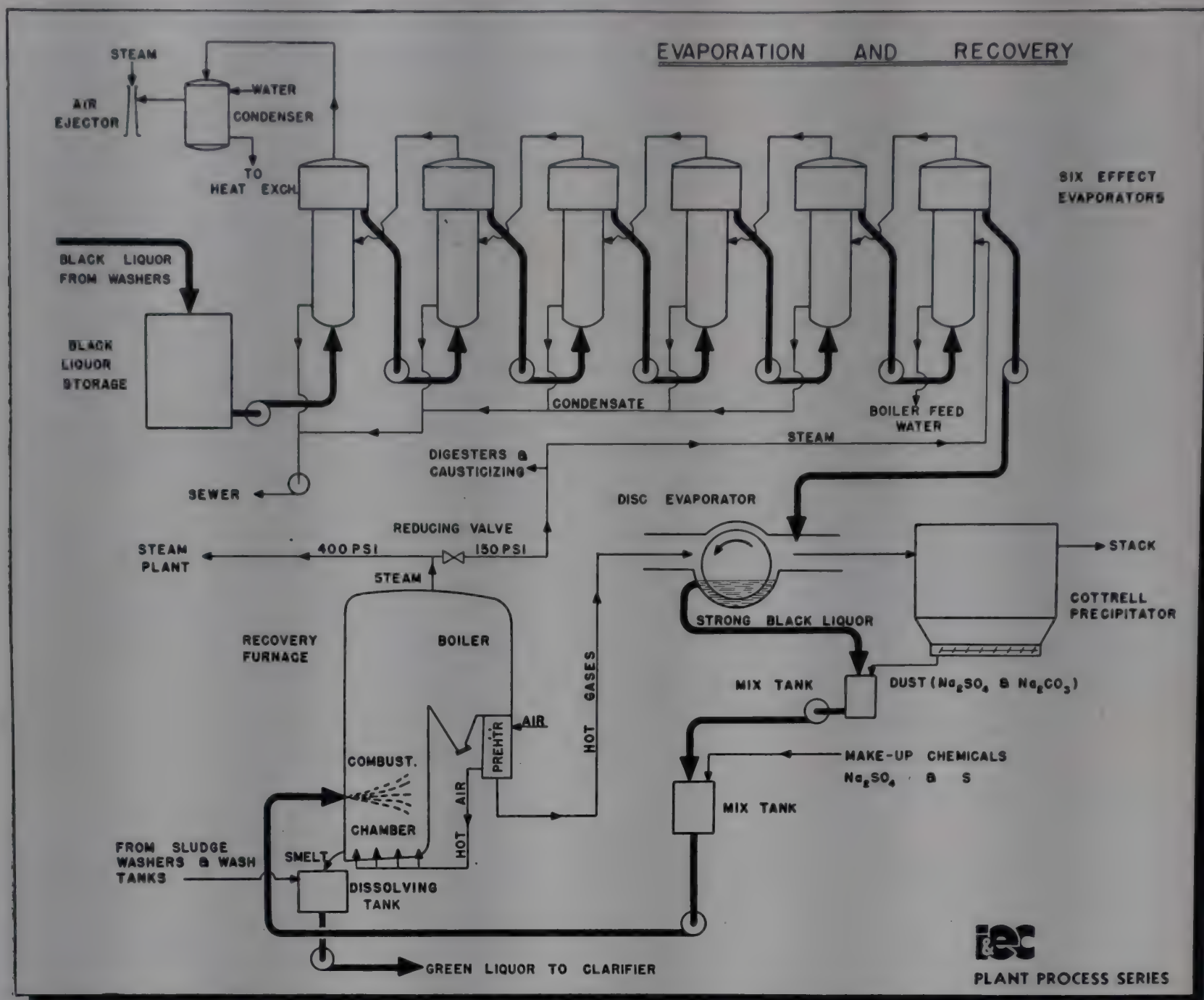


Figure 3. Evaporation and Recovery of Chemicals in Production of Kraft Pulp

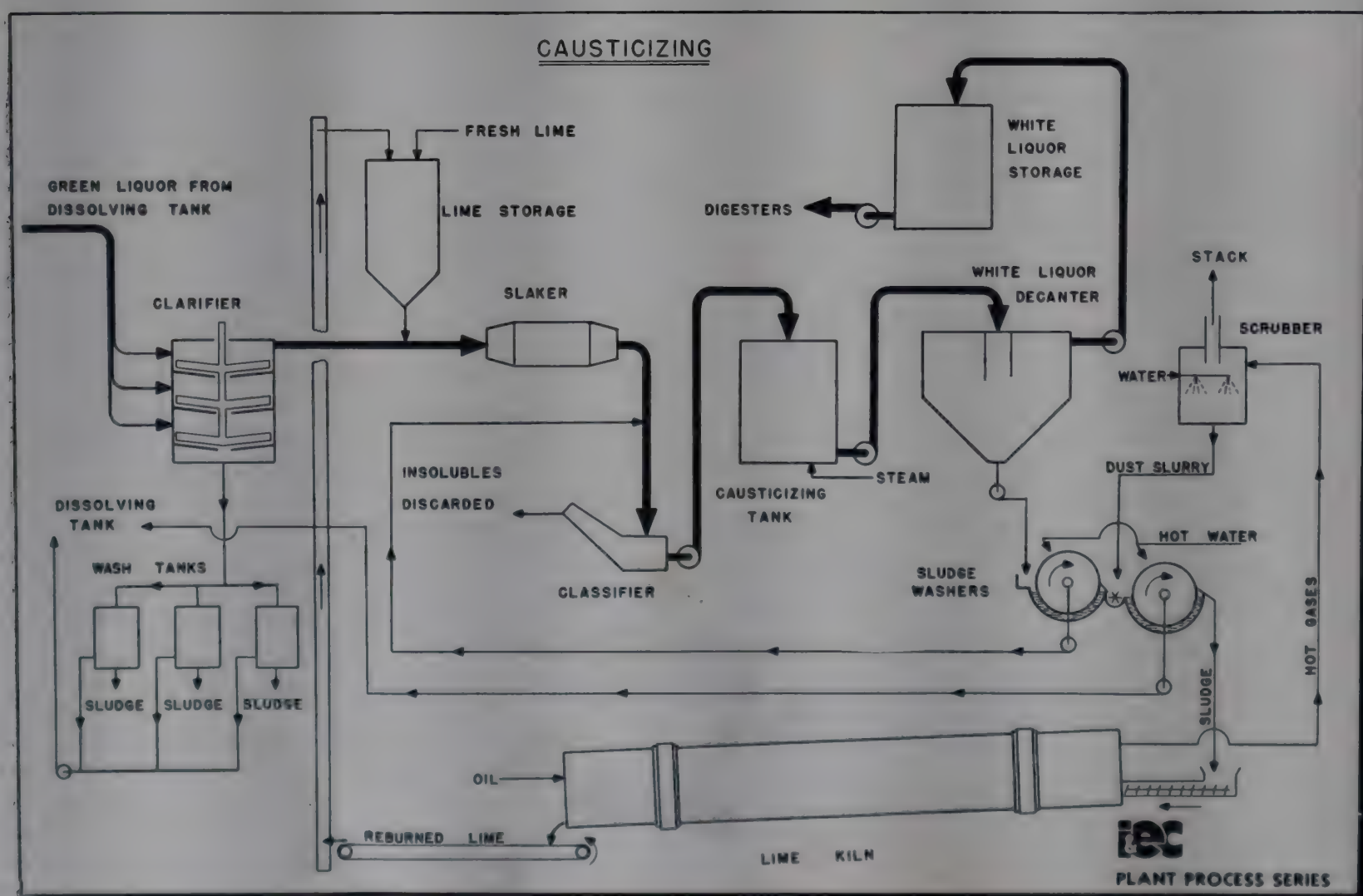
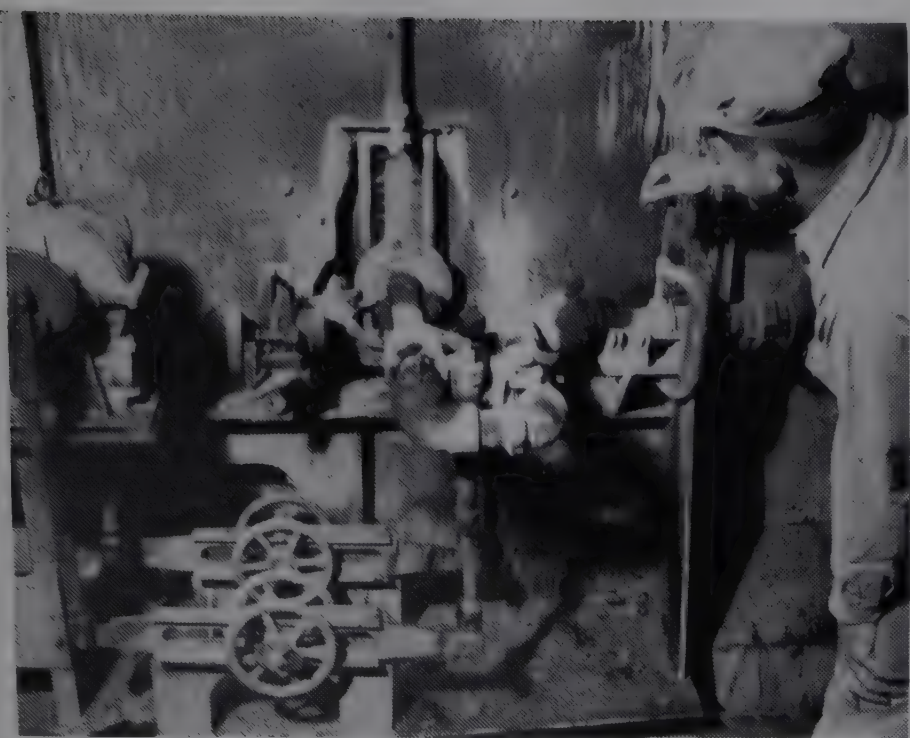


Figure 4. Causticizing Operation in Production of Kraft Pulp



Device for Oscillating Nozzle of Tomlinson Recovery Furnace

The furnace becomes a part of the waste heat boiler. The side water walls are carried under the hearth to the central mud drum and cool the refractory used to build up the sloping hearth of the furnace.

The boiler is a two-drum two-pass unit capable of generating 12,000 pounds of steam per ton of pulp at 400-pounds-per-square-inch pressure. The increased steam recovery is one of the chief advantages of this furnace. It was designed to burn 600,000 pounds of solids per 24 hours and produce 104,000 pounds of steam per hour. Before the furnace was installed, the kraft mill "bought" large quantities of steam from the central steam plant. This is no longer necessary. The recovery furnace supplies enough steam for cooking, evaporating the black liquor, and other smaller plant uses (Table V).

TABLE V. STEAM REQUIREMENTS

Use	Quantity of Steam Used ^a , Lb./Ton Air-Dry Pulp
Black liquor evaporation	3,400
Pulp digestion	3,100
Causticization	400
Furnace operation, feed water heating, plant heating, etc.	200
Excess steam to central steam plant	3,900
Steam generated in waste heat boiler of recovery furnace	11,000

^a The equivalent of 1600 lb./ton are recovered as hot water from the digester blow gases; this water is subsequently used for pulp washing, etc.

Air enters the furnace in the side and back walls through primary air nozzles located 2.5 feet above the hearth and through secondary nozzles 15 feet above the hearth. A centrifugal blower moves the air that passes through a heater before entering the furnace. This heater raises the air temperature to 380° F. Air flow to the furnace is controlled by raising or lowering dampers in the nozzles and also by varying the pressure at the blower. Excess air is avoided because it will oxidize carbon directly to carbon dioxide, thereby destroying its ability to reduce salt cake to sodium sulfide. Incomplete salt cake reduction lowers the amount of sulfide in the cooking liquor and increases the inert sulfate load.

For best operation, the air input is kept to not more than 105% of theoretical. Above this there would be increased carry-over (largely sulfate) which builds up boiler-tube-bank accumulations difficult to remove. There would also be irregular burning to the point of ignition loss. As the excess air is reduced, the concentration of sodium carbonate in the carry-over will be higher; there

will be incomplete combustion and reduced steam production. Successful operation of the spray-type furnace requires careful adjustment of air input within a narrow and critical range.

The liquor is sprayed into the furnace at 35 pounds per square inch pressure through a hardened steel nozzle $\frac{7}{8}$ inch in diameter. The liquor strikes a flat stellited surface deflector plate or distributor plate set at 50 degrees with respect to the line of liquor flow. The spray nozzle is given a two-directional oscillating motion so that the spray reaches all parts of the furnace walls. The size, angle, and oscillating motion are all critical to the efficient performance of the furnace in order to give the proper distribution of the liquor through the furnace for maximum evaporation of water prior to burning.

The spray nozzle is 10 feet above the hearth. The combustion chamber is 64 feet high, 15.5 feet wide, and 17.5 feet long. The liquor in passing through the chamber is partially concentrated so that it is in the form of large uniform sticky drops when it reaches the furnace walls. These drops adhere and are further dried out. This gradually builds perhaps a foot of char which then falls onto the hearth where it is burned by the primary air. Black liquor has a heating value of about 6500 B.t.u. per pound on a dry basis. The organic portion of this has a heating value of 11,000 B.t.u. per pound on dry basis. If the liquor were atomized instead of distributed as large drops, the organic matter would be oxidized directly to carbon dioxide by the secondary air. This would eliminate the reducing zone near the primary air inlet, thereby preventing formation of sodium sulfide, defeating one of the furnace purposes.

COTTRELL PRECIPITATORS

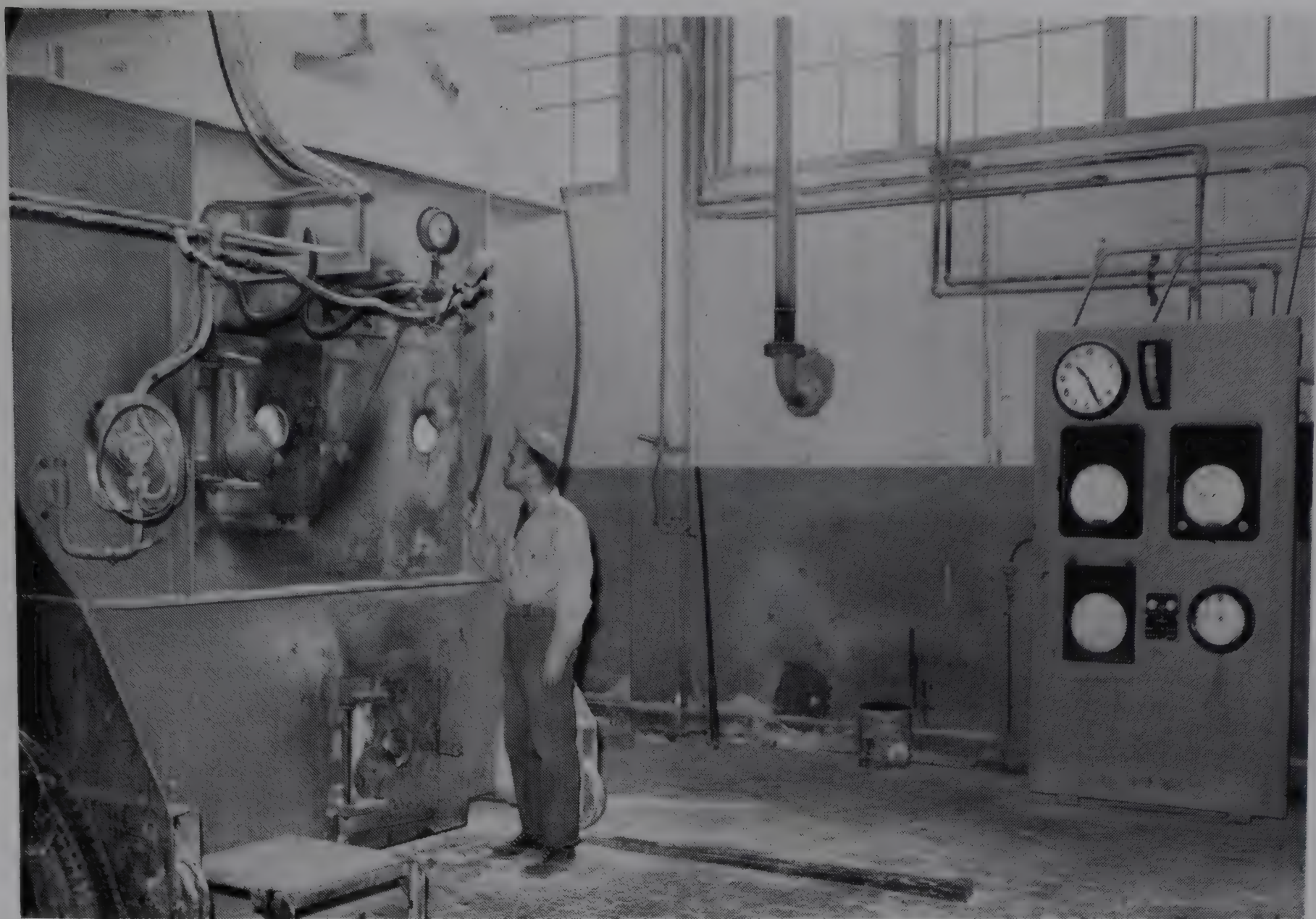
The hot gases (14.5% carbon dioxide, 0.1% carbon monoxide, and inorganic chemical dust) generated from burning the black liquor pass up through the furnace and boiler, leave an air heater at 410° F., go through an induced draft fan, are cooled to 325° F. in the disk evaporator, and enter at 320° F. four Cottrell electrostatic precipitators in parallel (18E). Two are 12 × 12 feet with a rated combined capacity of 65,000 cubic feet of gas per minute. Two are 12 × 18 feet with a rated capacity of 100,000 cubic feet of gas per minute. This is based on 95% precipitating efficiency. The larger units were necessary to take the increased load of a new recovery furnace built after the original two precipitators were installed.

Each unit is divided into three sections in series. The units are paired so that four mechanical rectifiers are used to step up the 440-volt inlet current to between 45,000 and 65,000 volts for the six sections of two units. One rectifier supplies the two inlet sections; another supplies the two inner sections. However, the two exit sections are supplied by two rectifiers. This makes possible a higher potential and thereby precipitates more completely the less concentrated suspended solids in the exit sections.

Particles in the gas carry a slight negative charge. While passing through the Cottrell this charge is increased until the particles are attracted to the positive or grounded pole. They are held there by physical forces until removed by a mechanical rapping device which knocks them into a hopper for removal by a screw conveyer. The dust, largely sodium sulfate and sodium carbonate (Figure 5), is returned to the recovery furnace to be reprocessed. For every ton of pulp produced, the Cottrells precipitate 100 to 120 pounds of dust.

The dust-free gases pass to a booster fan (capacity 133,000 cubic feet per minute) and then to a stack (150 feet high and 12-foot top diameter). An air-controlled damper after the booster fan maintains the Cottrell chambers at 0.2 inch of water vacuum.

While the char burns on the furnace hearth, the caustic soda, which was combined with the organic matter in the black liquor, is converted mainly to sodium carbonate. The salt cake and Cottrell dust that were added to the black liquor before burning are converted to sodium sulfide. Enough salt cake must be con-



Hot End of Lime Kiln

Operator is observing flame through cobalt glass

liquor is handled there is increasing use of stainless steel. Between the causticizing tanks and the decanter, pumps and piping are made of stainless steel Type 304.

Above 200° F. or in the presence of agitation, or both, any caustic solution is corrosive and stainless steel is desirable, but the high cost limits its use. Ordinary steel is used after the decanter. Although temperatures are above the critical point in the digester, the caustic concentration is low enough because of steam addition and reaction with wood so that ordinary steel gives satisfactory service. The stainless steel linings in six of the digesters have not been in use long enough to determine accurately their life.

LIME KILN

Lime sludge is withdrawn from the bottom of the decanters by pumps and sent to two vacuum filters (12E) in series (6 feet in diameter with 4-foot face). In the primary washer, filtrate from the secondary stage is used as wash liquor, and fresh water is used on the secondary stage. Sludge from the secondary stage drops on a screw conveyer which transfers it to the cool or feed end of an oil-fired rotary kiln (2E), 120 feet long and 8 feet inside diameter.

As the kiln rotates at 0.5 r.p.m., the sludge gradually moves through a chained section, then down to the front of the kiln, being "burned" by the intense heat. It finally emerges as "re-burned" lime which is used again for causticizing. This lime recovery is essential to economical operation. In the early days of kraft pulping, the sludge was dumped and new lime used. Without recovery, lime usage would be 500 pounds per ton of pulp. With recovery, lime make-up averages 30 pounds per ton of pulp.

Kiln operation is controlled by a radiation pyrometer (6E) in the hot or discharge end (2100° to 2300° F.) and a recording thermometer (11E) at the cool or feed end (400° to 600° F.). A

recording conductivity meter on the filtrate from the sludge filters gives the amount of soda left in the cake going to the kiln. It is important that this be kept between certain limits; otherwise, "ringing" occurs. This is caused by the tendency of lime sludge entering the kiln to stick to the walls in the form of rings which prevent the free passage of lime. Before installation of slaking and classifying equipment, much trouble was experienced. This has been licked by providing clean lime sludge, free of underburned lime, overburned cores, and other foreign matter.

Reaction occurring in the kiln is represented as follows:



At least 90 to 95% of the lime used in causticizing is recovered through the kiln and re-used. The balance of usage is made up with new lime.

It can be concluded that the manufacture of kraft pulp is largely a chemical recovery process. The recovery efficiency must be over 80% and with modern equipment should be about 90%.

This is accomplished with a low labor requirement. Only 1.5 man-hours are necessary to make 1 ton of pulp, air-dry basis. For a typical 330-ton day there will be 17 men in production on three 8-hour shifts, totaling 408 man-hours. To this are added: maintenance, 35 man-hours; laboratory, 16; supervision, 16; engineering, 12; and inspection, 8. All men work on a 5-day, 40-hour week.

A further breakdown shows that digestion and screening require two cooks, four helpers, and two men on screens and washers. The evaporators and Cottrell require one man; four men take care of the two recovery furnaces; one boilerman tends both units; and one man handles the chemicals. For the remainder of the process, one man is in charge of the sludge filters and lime kiln and one man makes the caustic liquor. On each shift there are

also a foreman and a pulp tester. One shift a day includes a laboratory tester, six maintenance men, a cleanup man, and an electrician. For special tests there may be an additional laboratory tester. There is also part-time service available from the general mill labor resources. Inspection is called "preventive maintenance" and is planned so that shutdown of equipment can be done on schedule instead of only in emergencies.

THE FUTURE

The Douglas fir region of the Pacific Northwest and the southern pine area of the Southeast are the two largest remaining sources of wood in the United States. It is natural to expect that the future of the pulp and paper industry will loom large in the economy of those regions.

The rapid growth in demand for kraft pulp shows no sign of slowing down. More sources of pulp will have to be found. These may result from improved wood waste harvesting, utilizing low grade wood and the less preferred species, and increasing pulp yields.

Statistically, there is enough suitable wood as saw mill waste, windfall, and logging waste in the area bounded by California, the Cascades, and Canada to more than supply all the needs of the pulp and paper industry of the area. Present economics militate against salvaging this wood because it is found in scattered and isolated locations.

New uses for kraft pulp will also be found. An example is the recent use of kraft for dissolving or nitrating. This had been impossible for years because of the noncellulosic impurities. During the past 10 years, German pulp technologists were able to prepare kraft pulp suitable for those purposes through a mild prehydrolysis with sulfuric acid. This opens up a new field for kraft pulp because the dissolving pulps constitute an increasing market as rayon consumption soars.

During the past 40 years the kraft process has been improved largely by refinement. In 1950 the fundamental process remains the same but costs have been cut, chemical recovery is more efficient, and the product is better because of controlled manufacturing conditions maintained through dependence on instrumentation instead of manual control. These and many more changes have all contributed to the conservation of our disappearing natural resource, wood. But these changes are not enough to ensure a vastly expanded future for the industry. The reason is based on fundamental wood chemistry.

The natural material comprises about 52% α -cellulose, 28% lignin, 15% hemicelluloses, and the remaining 5%, rosins, fats and extractives. In removing the bulk of the lignin of wood from a pulp, nearly one third of the cellulose is lost since only about 37% of the original wood is recovered in a good kraft pulp as α -cellulose. A summation of all the remaining possible refinements of method will not provide means for recovering all the α -cellulose. Since the aim in pulp making is to retain all of it that was present in the original wood, future developments must be based on some radically new approach. Economics demand it, since the cost increases as wood reserves are depleted.

Perhaps more important from a natural resource standpoint is the utilization of the noncellulosic part of wood. The most abundant unexploited organic by-product in the world today is lignin, which comprises about 30% of the weight of wood. In the manufacture of pulp by the alkaline processes, only heat is reclaimed from the lignin in the burned liquors. Few chemical uses have been found. These include: paper impregnant, molding powder, expander in lead-acid batteries, the ethers as film formers in protective coatings, the stearate as a mold lubricant, dispersing agent in asphalt emulsions, base exchange material, and a few other minor uses (4).

The market for any one of these uses could probably be satisfied by the output of one mill. The production of heat is the only



Vapor Heads of Sextuple-Effect Evaporators Showing Arrangement in Limited Space


current large scale use of lignin. This is a low grade of economic recovery and should be replaced by more profitable chemical products. There are 4,000,000 to 5,000,000 tons of lignin available each year in the United States from pulping processes. This is the incentive for a large and expanding field of research.

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Kraft Papermaking

Stock Flowing through Slice of Head Box onto Fourdrinier at Camas, Wash., Mill of Crown Zellerbach Corporation

FREDERICK G. SAWYER

Associate Editor

in collaboration with

CHESTER T. BEALS AND ARTHUR W. NEUBAUER

Crown Zellerbach Corporation, Camas, Wash.

THE story of paper is romantic and exciting. Its early history tells of Chinese scholars, an emperor, Arab conquerors, and merchant caravans. In the Seventeenth Century, the art of papermaking came to America.

In 1798, a French workman named Louis Robert announced that he had discovered a way to make, with one man and without fire, by means of machines, sheets of paper of a very large size, even 12 feet wide and 50 feet long. Robert secured a patent on his machine but did not have the money to finance it. Two wealthy London stationers, Henry and Sealy Fourdrinier, became interested in the proposition. In 1804, the first successful machine was started at Frogmore, England. The paper machine was named after the Fourdriniers because of their persistent faith which, however, led them to bankruptcy. After having spent £60,000 and being reduced to penury, they petitioned Parliament for compensation. Fortunately, their labors were appreciated and £7000 were voted them. Although their machine has been changed somewhat in details, it is still fundamentally the same as the one originally invented (6).

Now that mechanical means for making paper had been developed, it was soon realized that rags and straw were not available in sufficient quantities to sate the machine's voracious appetite. A new fibrous material had to be found. In 1850 a German named Frederic Kellar studied the pulp-making methods of the wasp, and with a mechanic named Henry Volter devised a machine for grinding wood into fibers. Two years later, Hugh Burgess, an English inventor, was issued patents for pulping by what is now known as the soda process. Man was improving on the wasp.

In 1865 American chemist C. B. Tilghman discovered the method known today as the sulfite process for cooking wood. In 1884 the kraft process was developed. Because of the great strength of kraft pulp, its production has greatly increased in recent years, particularly in the southern states and on the Pacific Coast. This process, as applied in the Camas, Wash., mill of the Crown Zellerbach Corporation, was described in a previous staff-industry collaborative report (14). The present article is a sequel describing how this same mill makes paper from kraft pulp.



Modern papermaking can be considered a chemical and engineering process. The importance of chemicals is emphasized by the fact that more than 600 are now used to improve pulp and paper quality and to build new paper characteristics. The pulp and paper industry is the third largest consumer of chemicals, following only fertilizer and rayon (15). The basic pulping chemicals used include caustic soda, lime, salt cake, soda ash, sodium sulfide, and sulfur. In the last 20 years, the use of these chemicals in pulp manufacture has increased at a rapid rate. For example, use of caustic soda has increased more than four times; chlorine has increased three times; soda ash almost three times; and salt cake seven times (13).

After the pulp is made, many more chemicals are needed to make it into a sheet of paper. These include alum, colors, starches, proteins, resins, and pigments such as clay, talc, titanium dioxide, diatomaceous earth, alkaline carbonates, and calcium and barium sulfates. At least 200 chemicals can be used for coating paper. Chemicals are also used for deinking paper and for making the sheet strong when wet. World War II showed dramatically that wet strength papers are here to stay. Chemical techniques have been applied to the improvement of paper packaging, including development of multiwall bags, resin-impregnated papers, resin coatings, waterproof adhesives, and special sealing compounds for bag closures.

CAMAS, WASH., MILL OF CROWN ZELLERBACH CORPORATION

Today we have all the necessary components to make kraft paper: the kraft pulp, the Fourdrinier machine, good water, chemicals, and skilled American manpower. These factors are combined efficiently in the Crown Zellerbach Corporation mill at Camas, Wash. Some idea of the Camas mill's size can be gained from its annual materials requirements shown in Table I. Although this plant makes a wide variety of pulps and papers, only the manufacture of kraft bag, wrapping, and specialty grades, such as waxing, food cartons, meat wraps, etc., will be discussed in detail. A summary of the general operations at Camas follows:

After being prepared (14), the kraft pulp or stock is stored at 17% consistency. When needed for papermaking, the pulp is diluted, screened, thickened (deckered), and sent either to the bleach plant for further processing or to the beaters.

A multistage process is necessary for bleaching kraft pulp in order to obtain the required degree of whiteness without weakening the fibers. Bleaching consists of removing lignin residues and the brown color. Chlorine is added and the subsequently formed insoluble chlorinated lignins are solubilized with sodium hydroxide. The pulp, finally whitened by hypochlorite treatment, enters the beater room parallel to the unbleached pulps.

TABLE I. CAMAS MILL ANNUAL REQUIREMENTS

Wood, board ft.	182,000,000	Lime rock (and dolomite), lb.	36,529,000
Water, gal.	23,785,800,000	Salt cake, lb.	11,860,000
Electricity, kw.-hr.	257,325,000	Alum, lb.	5,957,000
Lubricating oil, gal.	71,500	Lime, lb.	10,107,000
Grease, lb.	36,500	Rosin size, lb.	4,773,000
Steam, lb.	3,165,119,000	Pigments (clay, talc, titanium dioxide), lb.	4,587,000
Hog fuel, cu. ft.	34,358,000	Dyestuffs, lb.	476,000
Chlorine, lb.	16,554,000		
Fuel oil, barrels	210,300		
Sulfur, lb.	30,788,000		

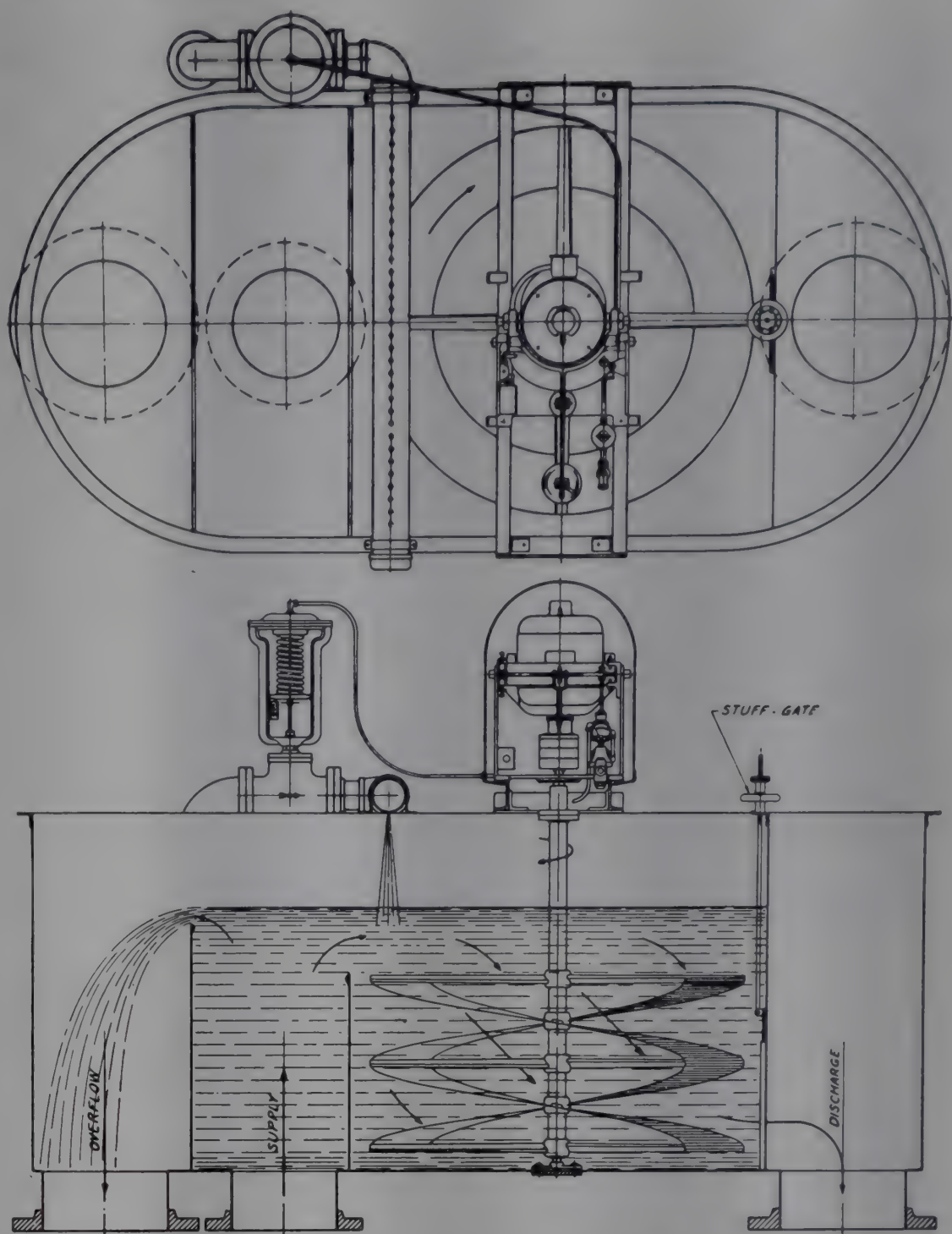


Figure 2. Consistency Controller

In the beater, the fibers are fibrillated (ends frayed) and bruised to develop strength characteristics in the subsequent paper. Some cutting also takes place. Chemicals such as colors, resins, size, and fillers are added.

From the beaters, the pulp passes through a series of refiners (Mordens and jordans) where for the most part the fibers are shortened to give further desired sheet characteristics. The stock is then metered, diluted, and introduced to the paper machine. Here it is distributed uniformly across a continuously moving wire cloth which allows water to drain through. Table rolls, suction boxes, and suction rolls aid this natural drainage.

The wet web is transferred to an endless woolen blanket which conveys it between press rolls to remove more moisture. There are also rolls in the press section to control sheet thickness and surface. This is followed by drying over steam-heated drums where the sheet is held against the drums by a continuous canvas felt. In the drying section there are also smoothing rolls and application facilities for surface treating or sizing. The sheet passes from the last heating drum through a calender stack for final machine finishing. It is then reeled and rewound to be either cut for shipment or subjected to further finishing.

STORAGE AND SCREENING

The manner in which the many materials are combined and processed to produce a specialty grade paper will now be considered in detail, as applied in the Camas, Wash., mill of Crown Zellerbach. The kraft pulp is stored in two high consistency chests (85 tons of air-dry fiber) made of red tile-lined concrete (Figure 1). The small amount of soda compounds (30 pounds per ton of pulp) in the pulp would eventually attack unlined concrete resulting in spalling. The tile lining ensures cleanliness of the stock and long life for the chests.



Figure 3. Pulp Running through Primary Screens

In order to remove the 17% consistency pulp for papermaking, water at 50 pounds per square inch pressure shoots in toward the center of the chest from a number of jets at the bottom. The lowermost pulp is washed to the center of the chest and down through two centrifugal pumps. The stock, now diluted to 2.5 to 3% consistency, is pumped to two 12-ton tile-lined concrete receiving chests. A 36-inch propeller type impeller agitates the stock by forcing it between two vertical walls which divided the chest into approximate thirds. The stock flows down the center channel; divides into two streams flowing behind the walls to the other end; then the streams converge and are forced through the impeller again. The splitting and converging of the two elliptical flows provide agitation. Flexibility of operation can be obtained by varying the pitch of the impeller blades. The same size impeller can be used in other chests with only an adjustment of the blade pitch to take care of consistency differences.

The stock is then pumped to a consistency controller (7E) where it is diluted to 1.5 to 2% (Figure 2). An overflow line returns excess stock to the receiving chest. In the consistency controller there is a central helical ribbon 30 inches in diameter and 8 inches wide. As the agitator is rotated at 50 r.p.m. by a 1.5-hp. motor, the upward reaction is related to the consistency at that moment. An increase in consistency produces greater upward thrust on the agitator, raising the unit, and thereby changing position of the pilot valve stem. This in turn opens the dilution valve to admit more water. A decrease in consistency causes the unit to lower, admitting less water. The controller cannot thicken but can dilute the incoming stock. The mechanism will control consistency within approximately 0.3% on either side of the setting.

The important removal of shives and dirt is accomplished in screens. The pulp flows to a head box where it is diluted to 0.6% (Figure 3). It subsequently flows to three rows of primary screens. Each row comprises three 14-plate screens pitched 0.5 inch to the foot. Rubber diaphragms under the screens are activated by four-point cams. The plates are made of chromium-plated bronze, 43 inches wide and 11³/₈ inches long, having narrow slots six to the inch with an opening of 0.012 inch (known

as 12-cut). Unplated bronze wears away too quickly and does not retain the slot shape. The screen plates are mounted on brass containers and are held in place with fasteners that can be easily adjusted and removed for inspection and cleaning.

The rejects (pulp, shives, and dirt) that do not pass through the slots of the primary screen are diluted to 0.3% consistency and pumped to the head box feeding two rows of secondary screens. These are similar to the primary screens but the slot openings are 10-cut. Rejects from the secondary screens are diluted to 0.2% consistency and pumped to one line of tertiary screens. These are similar to the others except that the openings are 8-cut. Rejects from the tertiary screens go to jordan refiners, then are screened and used for coarse wrapping grades of paper. The normal daily screen capacity is 180 tons, but up to 250 tons have been handled.

In the meantime, all the stock that passes through the slots in the primary, secondary, and tertiary screens is thickened on four deckers. The decker is simply a wire mesh-covered cylinder rotating in a tile-lined vat filled with screened pulp. The cylinder is 48 inches in diameter, 120 inches long, and rotates at a peripheral speed of 120 feet per minute. A partial vacuum maintained within the cylinder causes water to flow through the mesh and fibers to be retained on the surface. This stock at a consistency of about 4.5% is removed by a rubber-covered self-driven roll, called a couch (3). A rubber and asbestos doctor removes the thickened stock from the couch.

The stock is then diluted by showers to about 3.5% and run into two screened stock storage chests made of tile-lined concrete (25 tons of air-dry pulp capacity). These are agitated as in the previous stock chests. From these chests the pulp can be pumped either to the kraft bleach plant or to the beater chests.

BLEACHING

All wood pulp, no matter how carefully made, has associated with it some lignin and certain color bodies of highly complex chemical nature. To make the brighter grades of paper, bleaching is necessary. This is done in two major steps: the lignin remaining from the digestion process is removed by treatment with chlorine and sodium hydroxide; and the brown color associated with kraft cooked pulps is bleached by calcium hypochlorite. The latter is the most expensive of the bleaching chemicals. It is also least selective and most harmful to the pulp strength. Based on these facts, the Camas bleach plant is designed to produce a pulp fairly free of lignin before hypochlorite is used (Figure 4).

Process flexibility is essential for coping with the various colors and wood species handled. A system of three-way valves and pipes along with the necessary chemical treatment equipment makes it possible to change the bleaching sequence in several ways. Any of the stages can be skipped, thereby using only that number needed for the particular grade and process.

TABLE II. PROCESS VARIABLES FOR FULLY BLEACHED KRAFT (80 G.E.)

	Cl ₂ , %/Ton Air-Dry Pulp	NaOH, %/Ton Air-Dry Pulp	pH at End	Temp., ° F.	Con- sistency, % Air Dry	Reten- tion Time, Min.
4-Stage system						
1st chlorination	7.0	0	2	Cold	4.0	60
1st hypochlorite	4.5	1.9	7.5	90	13.3	30
1st caustic	0	2.1	8	160	11.0	60
2nd hypochlorite	1.2	0.3	7.5	90	5.5	210
8-Stage system						
1st chlorination	7.0	0	2	Cold	4.0	60
1st caustic	0	4.0	8	160	11.0	90
Soak	0	0	7.5	Cold	3.3	60
2nd chlorination	1.3	0	3	Cold	3.3	60
2nd caustic	0	1.3	8	140	11.0	90
1st hypochlorite	1.7	0.3	7.5	90	13.3	210
2nd hypochlorite	0.1	0	7.5	90	5.5	180
SO ₂ flash	0	0	5.5	Cold	3.3	60

Pulp specifications in this connection are based on a standardized reflectivity or brightness as measured by a General Electric brightness tester (14E). The higher the reading on the 0-100 instrument scale, the brighter or more completely bleached is the pulp. This instrument uses a specially prepared magnesium oxide as a full scale standard of 100. On this scale, "full bleached" pulp will fall between 80 and 90.

When semibleached pulp (30 G.E. or 65-70 G.E. brightness) is being made, more than half the plant is by-passed. For instance, 30 G.E. pulp requires only one-stage bleaching with high density hypochlorite. The higher grades of semibleached kraft are bleached in three stages: chlorination, caustic extraction, and hypochlorite treatment. Fully bleached kraft pulp (80 G.E.) is normally done at Camas in four stages (Figure 4).

Additional bleaching stages have been built into the plant so that, if desired, an eight-stage fully bleached high purity kraft can be made. These stages consist of a low consistency chlorination; high consistency caustic treatment; water soak; second low consistency chlorination; second high consistency caustic treatment; high consistency hypochlorite treatment; low consistency hypochlorite treatment; and for final whitening, treatment with sulfur dioxide. Rotary drum washers are provided between each of these stages to remove impurities before undergoing subsequent treatments.

As an example of common practice at the Camas plant, a four-stage process is described in detail (Figure 4). Statistics are based on daily production of 150 tons of fully bleached 80 G.E. kraft pulp (Table II).

The pulp is pumped from the brown stock storage to a consistency controller (24E) and a recording stock meter (26E), which measures the production rate for the bleach plant. The stock is mixed (27E) with chlorine gas, then enters the bottom of a tile-lined concrete chlorinating tower where it is agitated by rubber-covered arms on a central top-driven vertical shaft.

The stock issuing from the top of the tower is pumped, washed (25E), and thickened to 17% consistency by squeeze rolls on the washer cylinder (Figure 5). A 3.5% sodium hydroxide solution is added immediately after the last squeeze roll to neutralize the stock and prevent the hypochlorite from going acid in the subsequent stage.

The stock drops into a two-tier double shaft high density mixer (28E) where calcium hypochlorite solution (0.31 pound of chlorine per gallon) is added. The pulp color is broken down by oxidation in the first hypochlorite tower (tile-lined concrete). A rubber-covered scraper agitates only the bottom pulp. A variable speed screw discharge (29E) forces the pulp into a chest where water dilutes it to pumping consistency.

The pulp is washed, thickened, and discharged into the first caustic tower, which is identical to the first hypochlorite tower. A 3.5% sodium hydroxide solution is added at the mixer. After being retained for 60 minutes, the stock is diluted in the dump chest and pumped to the third washer where it is thickened and dropped into the second hypochlorite tower. This is similar to the first hypo tower, but its larger capacity permits a longer retention time. The stock is diluted in a dump chest and pumped over the final washer and transferred to the bleached kraft stock chest. From here it enters the beater room parallel to the unbleached stock.

Process variables for making 80 G.E. brightness stock in both four- and eight-stage systems are compared in Table II.

The operation of a bleach plant is continuous so it is apparent that any change in stock consistency or bleachability (21) must either be corrected at once or compensating chemical treatment started. Tests used for control are consistency, bleachability, pH, and residual chlorine. Flow rates of chlorine, sodium hydroxide, and calcium hypochlorite are measured by area-type meters (9E). Instruments record temperature, flow rate, and pressure.

BEATING AND REFINING

A major part of the transition between pulp and paper takes place in the beater (19E). Although it has been eliminated in some newsprint and kraft mills in favor of other types of re-

finers, the beater remains in most mills as the machine that "makes" the paper. Just how this comes about has been the subject of many theories since the first Hollander beater was invented about 1680 (16). Nobody really knows exactly what takes place during beating or why. The only way to tell what the beater or refiners are really doing is to see what effects they have on the character of the paper made from the stock. This is admittedly a circuitous way to control such an important function (17).

The present tendency is to consider beating as effecting physical rather than chemical changes in the pulp. Among those postulated are: fibrillation; decrease in thickness of cell wall due to removal of fibrils; transverse cutting (shortening); collapsing of fibers; longitudinal splitting of the cell wall, resulting in opening up fibers as ribbons; decrease in fiber stiffness; and decrease in rate of drainage of water through mats of fibers. Paper made from beaten fibers will be stronger, less opaque, or of more uniform formation; it will have greater density, because of greater shrinkage of wet web, and thus be less porous (9). The first six of these changes can be observed microscopically. Many researchers claim that there is some interaction between water and the fibers. This so-called hydration can be interpreted in many ways. Pulp and paper vocabularies, textbooks, and technical papers are rife with ambiguous terminology. Perhaps semantic as well as scientific research is needed to clarify many problems of the industry.

When has a stock been beaten sufficiently to give optimum qualities to a particular grade of paper? The answer to this question is largely previous experience. There are tests of stock freeness and slowness which indicate rate of water drainage on the paper machine wire, but these do not tell the whole story. According to Sutermeister (17):

There is no beater control test of general applicability, and the only way to tell the condition of the stock is to make it into sheets under carefully controlled conditions and test them for their physical characteristics. Even this is subject to so many influences that results in different plants are not strictly comparable. It would seem that in spite of all the study given to it, beating is still an art, and not a science.

Figure 6 shows the principal parts of a beater. A heavy hollow iron roll is fitted around its periphery with sharp steel fly bars. Wedge shaped wooden segments are driven between the bars and when swollen with water hold the bars firmly in place. The bedplate is either stone or steel, the former is generally used for beating kraft. Most of the fibrillation takes place between the fly bars and bedplate. The roll is set on a spindle across the tub made of tile-lined concrete. The backfall is concrete covered with metal. A doctor prevents too much stock from being carried completely around the roll as this would reduce circulation and cut capacity. The stock circulates around a mid-feather in the center of the beater. The washer is an octagonal hollow screen covered with bronze cloth. During "washing" it is lowered one third of its diameter into the pulp; water flows through the screen, is scooped up by internal baffles, and discharged through a hollow shaft. This makes possible rapid increases in consistency.

Stock from the bleach plant, or unbleached stock directly from the decker chests following screening, arrives in the beater at 2.5 to 3% consistency. It is thickened to 5 or 6% in 10 minutes while the beater roll is up off the bedplate. Then the washer is raised and the roll lowered to the desired distance above the bedplate. Previous tests determine what surface speed of the roll will give maximum beating consistent with power consumption. Speeding the roll beyond this point accelerates the beating rate, but power demands are not proportional to the results obtained. Estimates indicate that above 60% of the power consumed is used just in circulating the stock (4).

The beating cycle for most kraft pulps is from 30 to 60 minutes. During this period, the beater also serves to mix any added

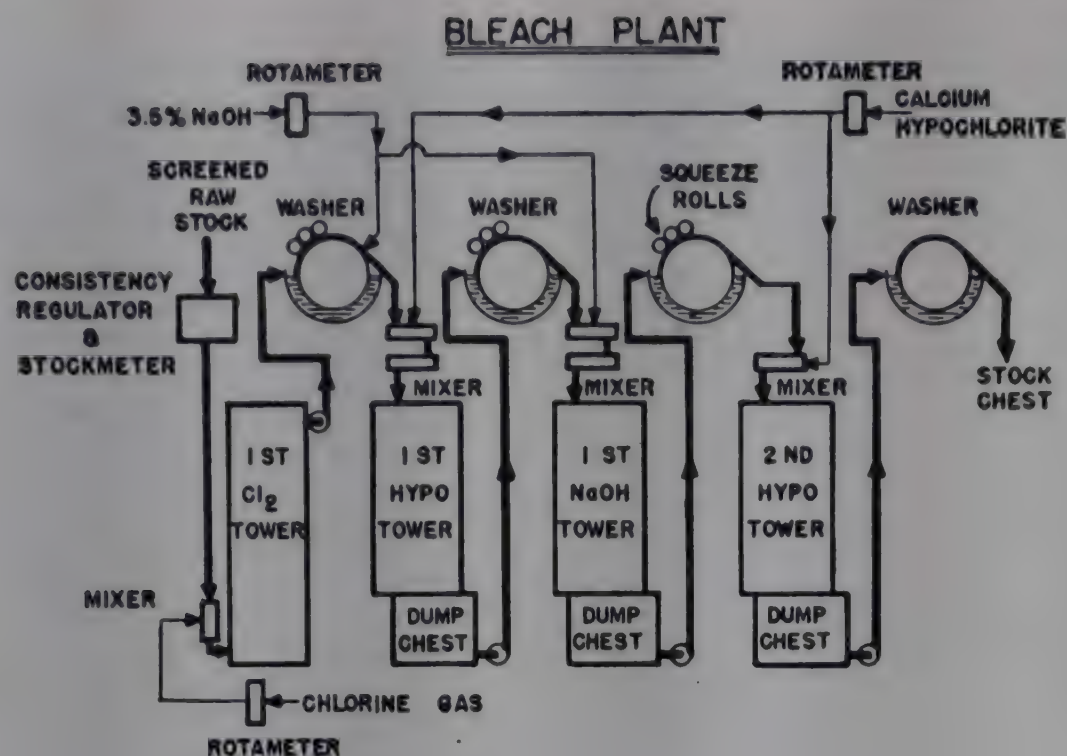


Figure 4. Bleach Plant

chemicals. The two most commonly used are rosin size and papermaker's alum.

Rosin size is purchased in tank cars as a thick paste (80% solids) and prepared for beater addition by heating to 170° F., then running through an ejector where it is mixed with hot water and emulsified. The 8% solids emulsion is further diluted with water to 4%, at which concentration it is furnished to the beater. This size averages 25% free rosin acids with the remainder saponified.

Rosin size increases the resistance of paper to penetration by liquids such as water, ink, meat juices, and paste. Besides there being a number of theories on sizing (18-20), the very word "sizing" seems to mean all things to all men.

It is not the purpose of this article to discuss in detail the theoretical aspects of any particular phase of papermaking, but rather to show the application of chemical engineering principles in a particular modern kraft mill.

Certain hard-sized sheets require more than the normal amount of sizing. A high free-rosin size (colloidal free rosin acids protected by protein) is a more effective agent than ordinary rosin size. A wax size emulsion may be used as a supplement for beater addition. The latter is bought as 50% solids and diluted with cold water to 0.5 pound per gallon (6%).

Loading pigments may be added to the beater stock. These include clay, talc, titanium dioxide, lithopone, and extended pigments (titanium dioxide coprecipitated with barium or calcium sulfate). Titanium dioxide and the extended pigments are necessary for brightening and opacifying waxing grades. These may also be used for brightening other grades, but less expensive materials such as clay, lithopone, and talc are preferred. For the cheaper writing papers, clay or talc opacifies and improves the writing surface. Addition of any pigment gives the paper more pliability and less rattle and resiliency.

Colors for paper are added in the beater after loading. Many types of aniline dyes (basic, direct, acid) may be used. These are added as concentrated solutions or in powdered form to be dispersed under the beater roll. The addition of any dye decreases the paper brightness, in spite of the apparent opposite effect when, for example, blue is added to white paper. Other colors used in minor quantities are the earth dyes (sap brown), certain chrome colors, and carbon black.

Papermaker's alum is $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. It is added to the stock in the beater to precipitate the size and to set certain colors through adjustment of the pH. The retention and tint of many

aniline dyes are affected by pH. For heavily loaded or pigmented sheets, the colors are best retained at a pH below 5.5. For economic reasons and to avoid paper embrittlement, the pH is kept above 4 in the system.

If more alumina is required for setting the size without a concomitant lowering of the pH, sodium aluminate may be used. In the grades of paper made at Camas, it would be too expensive to use iron-free alum. Ordinary technical grade suffices. This is in contrast with mills making fine paper grades which would be darkened or otherwise adversely affected by traces of iron. For certain grades at Camas, a portion of the alum is added later at the stuff box, just ahead of the paper machine (Figure 1).

At the end of the beating cycle, the roll is raised and the stock dumped through a trap door (just ahead of the roll) and into a rectangular tile-lined first primary beater chest (capacity 8 tons air-dry stock at 3.5% consistency). Internal construction with impeller agitation is similar to that of the receiving chests ahead of the screens.

The stock is pumped from the first primary beater chest through two refiners (21E) in series (Figure 8) to supplement beating and then into a second primary beater chest. Now the stock leaves the beater room and travels 200 yards to the paper-machine building where extra storage capacity is provided by a secondary beater chest identical with the others. The stock may be pumped through two more refiners (21E) in series and then to the machine chest, also identical with the previous three chests.

After passing through a consistency controller (7E), the stock is divided and passes through two to four jordan refiners (18E) depending on the grade being made. Figure 7 shows the internal construction. A central plug fitted with bars or knives turns inside a similarly fitted shell. Usually the knives in both shell and plug are slotted, keyed, or banded to the casting, and the space between them is filled with wood strips driven tight and swelled with water before the plug and shell knives are faced to true cones. Stock enters at the narrow end of the cone, passes between the whirling knives, and the centrifugal action forces it out the larger end.

Jordan refining can be changed in character and degree by adjusting the clearance between the plug and shell; changing the speed; changing the composition, width, and arrangement of the

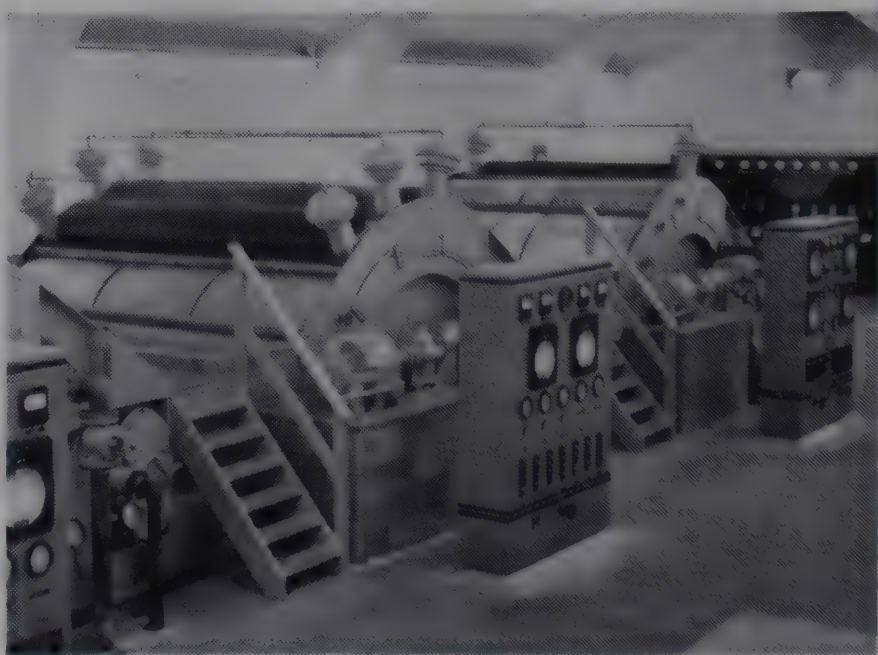


Figure 5. Washers and Squeeze Rolls in Bleach Plant

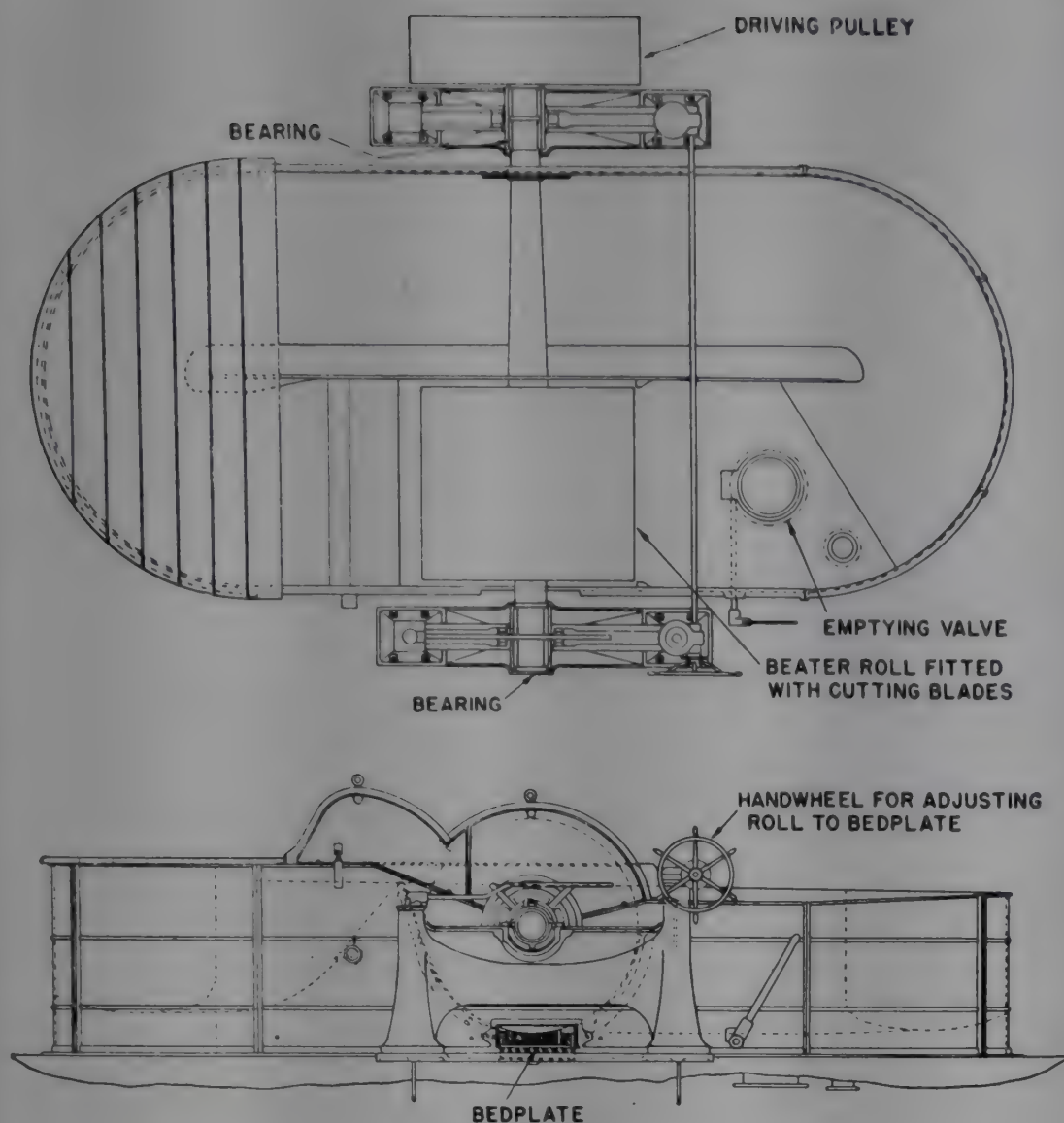


Figure 6. Principal Parts of Paper-Stock Beater

bars; changing stock consistency, hydrostatic head on the stock in the refiner, and the temperature. Practice is moving toward higher speed and higher consistencies. Speeds range from 300 to 550 r.p.m., which give the large end of a 30-inch diameter plug peripheral speeds of 2300 to 4500 feet per minute. This is nearly twice that of beater rolls (10). Stock or stuff consistency to jordans is usually 3 to 3.5%. Looking toward higher capacity, with stronger jordan designs and better application of power, consistencies tend to move upward. In the interest of sheet formation, with improved bearings, dynamic balance, and stronger materials, speeds also tend to move upward, since high speeds affect formation with less slowing of stock than slow speeds.

Jordans are primarily designed for cutting action on the fibers and should not be overloaded by doing the work of hydration best accomplished in the beater. Bronze knives or bars remain sharp on the leading edge and have more of a cutting action on the fibers, whereas steel bars tend to round over on the edges producing a brushing action. Monel metal bars have an intermediate effect (4).

At Camas, the jordans accomplish the final cutting and refining prior to the paper machine. Operation of the jordans is under the jurisdiction of the paper machine tenders who use this means to develop and control the final strength of the pulp.

The stock is pumped to the stuff box where the basis weight of the final paper is controlled. The stuff box has three compartments. The stock from the jordans enters the center one. An adjustable gate at the exit end allows just enough flow for the particular sheet

of paper being made. Excess stock from the jordans overflows into the third compartment and is returned to the machine chest (Figure 1).

Many materials that are important in establishing the final paper properties may be added at the machine stuff box. Certain characteristics of machine operation—for example, drainage through the wire and pH of the final sheet—require close control of the pH. Experience shows that the instrument-controlled (6E, 22E) addition of alum at the closest possible point to the paper machine provides the very narrow range of pH necessary for stock going to the machine.

Cooked starch solutions may be added at the machine stuff box to increase the dry bursting strength of the paper. Figure 9 shows the flow sheet and equipment used to add the starch solutions either at the machine stuff box or later on the paper machine size press. Temperature and liquid level are recorded in the mix tank. In each of the storage tanks the temperature is recorded and controlled and the liquid level is indicated.

Melamine-formaldehyde resins may also be added at the stuff box if high wet strength characteristics are desired in the finished sheet (1, 7, 8). Equipment used is similar (2) to that of the starch system with the following differences: A small amount of hydrochloric acid is added to the mix tank; the dilute resin colloidal suspension is stored in four 3000-gallon tanks without steam lines; only one transfer pump is used between storage and the 200-gallon supply

tank; the resin is applied to the stock in the machine stuff box only, not at the size press.

From the stuff box, the stock usually goes directly to the fan pump (40E) where the consistency is reduced from 3 to 0.3 to 0.5% by addition of white water. This is the water that drains through the mat of fibers on the paper machine wire. It is called "white water" because of its milky appearance which is due to suspended fine fibers and other solids. Because of the extremely high dilution of the stock at this point, the fan pump (40E) must be of high capacity—250-hp., 500-r.p.m., 13,000-gallons-per-minute, 40-foot head.

If metallic and other foreign particles are objectionable in the finished sheet, the stock may be passed from the stuff box and through an auxiliary mixing pump (41E)—125-hp., 700-r.p.m., 10,000-gallons-per-minute, 40-foot head. Here the stock is diluted with machine white water and then passes through a series

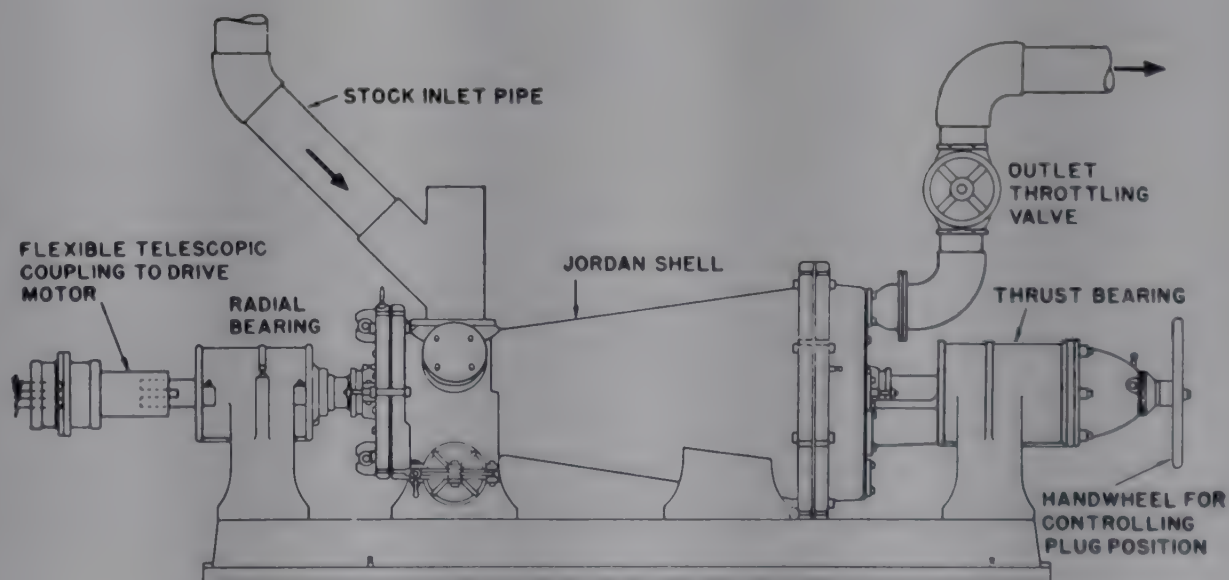


Figure 7. Jordan Refiner

TABLE III. ROLLS ON FOURDRINIER PAPERMAKING MACHINE

Location on Machine	Material of Construction	Diameter, Inches	Face, Inches	Crown, Inch
Rectifier rolls in headbox (2)	Rubber covered	12 ¹¹ / ₁₆	145 ¹ / ₂	...
Breast roll	Brass covered	25	156	...
Table rolls (32)	Micarta	8	156	...
Dandy roll	30-Mesh bronze wire covered	24	156	...
Suction couch rolls (2)	Cast perforated bronze case	30	156	...
Return wire rolls (5)	Brass covered	12 ¹⁵ / ₁₆	155 ⁵ / ₈	...
Wet felt carrying rolls (14)	Rubber covered	11 ¹ / ₄	164	...
1st press top roll	Rubber covered (Plastometer 45)(31E)	28	157	0.070
2nd press top roll	Stonite	28	157 ³ / ₄	0.015
1st and 2nd press bottom suction rolls (2)	Rubber covered	28	163 ¹ / ₂	0.040
Smoother press top roll	Rubber covered (Plastometer 21)	28	157	0.013
Smoother press bottom roll	Stonite	27	157 ¹ / ₂	0.015
1st section paper and felt dryer rolls (24)	Cast iron	60	154 ³ / ₄	...
1st section dryer felt carrying rolls (39)	Steel	11 ¹ / ₄	154 ³ / ₄	...
Spring rolls (5)	Brass	12 ²⁷ / ₃₂	155 ¹ / ₂	...
Marking press top roll	Rubber covered (Plastometer 8-10)	28	157	0.012
Marking press bottom roll	Steel	28	149	0.012
2nd section paper and felt dryer rolls (15)	Cast iron	60	154 ³ / ₄	...
2nd section dryer felt carrying rolls (30)	Steel	11 ¹ / ₄	154 ³ / ₄	...
Size press top roll	Rubber covered (Plastometer 24-25)	27	157	0.024
Size press bottom roll	Rubber covered (Plastometer 14-15)	28	157	0.011
3rd section paper dryer rolls (11)	Cast iron	60	154 ³ / ₄	...
3rd section dryer felt carrying rolls (23)	Steel	11 ¹ / ₄	154 ³ / ₄	...
Calender bottom rolls (2)	Cast iron	28	149	0.015
Calender rolls other than bottom (14)	Cast iron	15	144	...
Reel drum	Cast iron	36	144	...

of Dirtecs (3E). Foreign particles heavier than normal stock fibers are separated by centrifugal action as the stock spirals up long narrow cylinders. Only enough units are used to give optimum separation or removal of dirt. Stock from the Dirtecs passes to the main fan pump where additional white water brings the consistency down to 0.3 to 0.5%. A series of supplementary screens is available (4E).

THE FOURDRINIER PAPER MACHINE

The diluted stock enters the paper machine head box (1E) by means of distribution pipes entering each end. The head box quiets the flow and ensures uniform distribution of fibers by means of a series of internal baffles and rectifier rolls, which are perforated, rubber-covered, and rotate at 20 to 30 r.p.m. in the stock.

The stock flows from the head box, across a rubber-covered cloth apron, through an adjustable rectangular orifice—the slice shown in title photo—and onto the Fourdrinier paper machine wire directly over the breast roll. Figure 10 shows details of the No. 15 Fourdrinier at the Camas mill. All subsequent data refer to this specific machine (2E).

The Fourdrinier "wire" is a fine mesh bronze wire continuous cloth, 60 × 44 mesh weave, 152 inches wide and 105 feet long (periphery), which passes over the breast roll to pick up stock flowing through the slice. The linear speed of stock flow should be about the same as that of the wire. If the stock moves too fast, rolling of the fibers takes place to form a square or nondirectional sheet. This has poor appearance and may be undesirable in certain converting operations, such as cutting. If the stock flow to the wire is too slow, there will be drag of the fibers producing a highly unidirectional sheet that splits easily and would not be good for paper bags, for example.

Stock flow onto the wire is controlled by the opening of the slice and the stock level in the head box. To speed up the flow, either the slice can be narrowed or the stock volume increased in the head box by adding more white water at the fan pump. This lowers the consistency since the amount of pulp coming from the stuff box is uniform. Adjustment of the slice is very delicate, and the general sheet characteristics (tensile, tear, burst, formation, and basis weight) are very sensitive to small changes in slice settings. Unequal distribution of stock coming through the slice can be corrected by varying short increments of the 146-inch flexible stainless steel bar that comprises the slice.

About half the length of the machine wire is supported on a series of thirty-two table rolls followed by seven suction boxes. This constitutes the section on which the wet web or sheet

is formed. (Data describing all the different Fourdrinier rolls are included in Table III.)

As soon as the stock flows onto the wire, white water drains through by gravity, leaving a wet mat on the wire surface. Because of surface tension, the table rolls also aid in drawing water from the sheet. Resting lightly on the wire near each edge is a narrow strip of stainless steel with rubber lip. These "deckle" strips extend for about half the length of the table roll section and prevent the pulp from flowing off the edge of the wire during the initial stages of sheet formation. Sidewise oscillation of the breast roll and table roll section shakes the wire perpen-

dicular to its direction of travel. This improves the fiber distribution or formation of the sheet. Metal strips called deflectors are placed between each of the first six table rolls to divert the heavy flow of white water into the wire pit.

When the sheet reaches the suction or flat-box section, most of the free water has been removed. A vacuum (6 to 8 inches of mercury) pulled on these six stainless steel maple-faced boxes draws more water (about 25% of the total) out of the sheet and through ⁵/₈-inch round holes (rows 0.75 inch apart set on 1-inch centers). The suction boxes move eccentrically at 2.5 cycles per minute to eliminate any local vacuum irregularities that would affect the sheet formation and also to avoid wire drag.

A dandy roll, consisting of a light cylindrical frame covered with a bronze wire of mesh similar to the machine wire, runs free on the top of the sheet after the second suction box and is supported by a table roll. It improves the formation, smooths the sheet, reduces the fuzz, and prevents sticking on the first press roll. Immediately following the suction boxes, the wire travels over two perforated suction couch rolls (18 inches of mercury vacuum) which remove more water from the sheet. These rolls, known as the primary and main couches, drive the wire and therefore do not exert the frictional drag typical of the suction boxes. The sheet is removed from the wire at the main

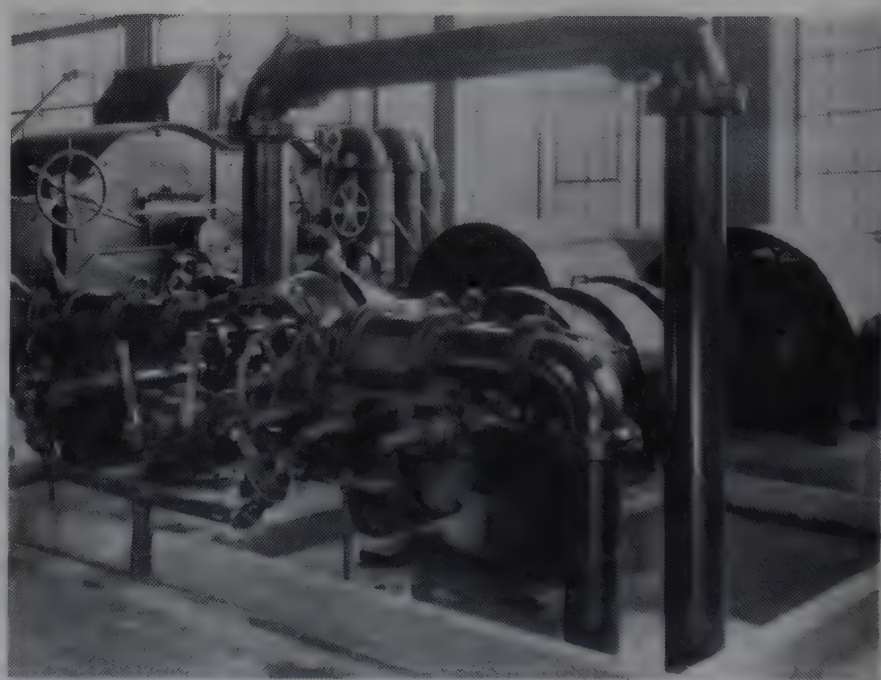
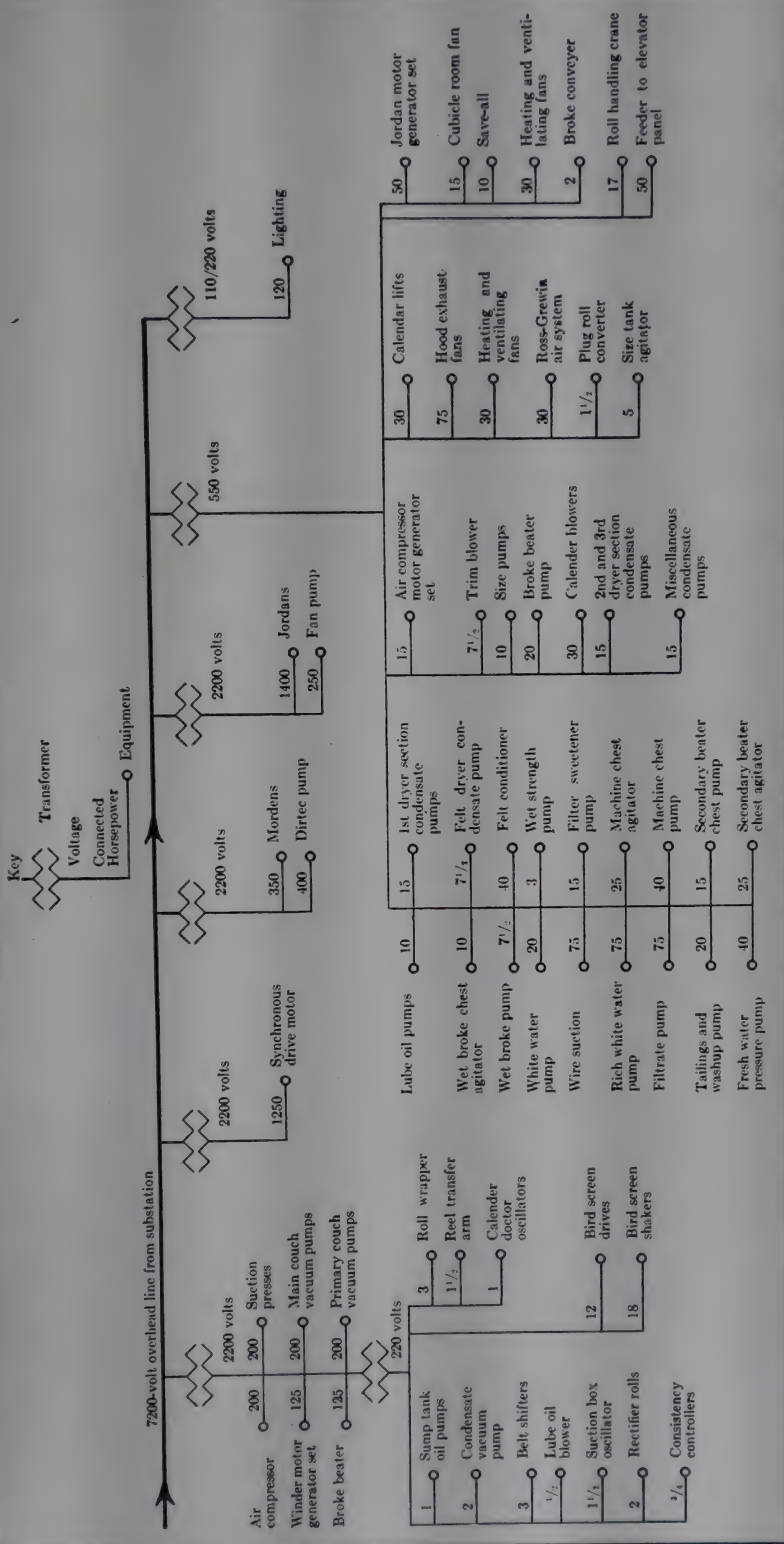


Figure 8. Two Morden Refiners in Series; Beater in Background

TABLE IV. ELECTRICAL SYSTEM FOR No. 15 FOURDRINIER



couch and transferred to the first press wet felt (wool blanket) which transports it through the subsequent press section.

After the wire leaves the main couch, it passes over a series of supporting return wire rolls back to the breast roll under the slice (Figure 10). One of the supporting rolls is mounted on a movable bracket to permit adjustment of wire tension. All rolls must be furnished with showers and doctors to prevent wire damage caused by stock collecting on the roll surfaces.

After leaving the wire, the wet sheet is carried on wet press felts through two sets of suction press rolls to remove more water. Effort is made to remove as much water as possible in the press section since evaporation of water by steam in the dryers is more expensive. The limiting factor in mechanical water removal by presses is the point where loading of the rolls "crushes" the sheet.

The sheet on the wet felt is passed between the nips of the first press rolls. Both are rubber-covered and the bottom one is perforated for suction. The sheet is transferred via a second press wet felt to two press rolls similar to the first pair.

At the same time, the two wet felts travel over a series of wet felt carrying rolls, one of which is provided with a movable bracket to adjust the tension. Suction boxes condition each felt by removing water, bringing out the surface nap, and cleaning the surface of wax and size.

From the second suction press, the sheet passes through a smoothing press without felt support or cushion which gives a certain amount of finish to the surface. The sheet (at about 65 to 70% moisture content) is now ready for the 1st dryer section.

Something should be said here about roll design. In order to keep the sheet of paper uniform, it is necessary to "crown" a single roll, or the lower roll of a pair, by making its diameter in the middle just enough larger than at the ends to make up for

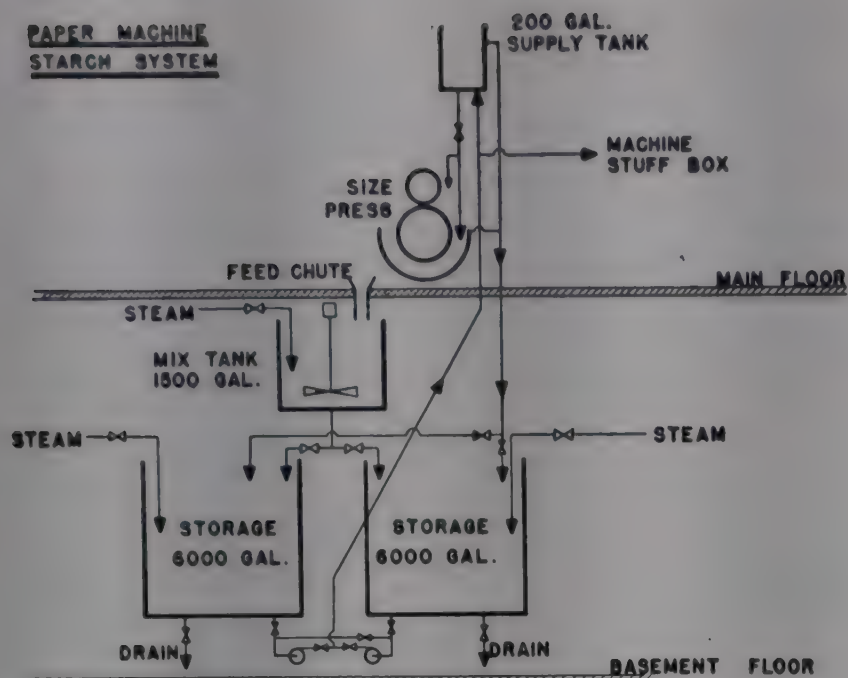


Figure 9. Starch System

the sag in the middle caused by the weight carried by the roll in the machine (11). Table III indicates the crowned rolls on the Fourdrinier.

It is important here as elsewhere on the machine to have the draw carefully adjusted. "Draw" is the tension (stretch) on the paper as it passes from one section of the machine to another. There must be a certain tension, or draw, between couch rolls and the first press rolls, between the press sections, the last press and dryers, between dryers and calender, and between calender and reels. The term is especially applicable to the wet end of the Fourdrinier where the paper gets most of its longitudinal stretching, which is caused by each press running more rapidly than the preceding one (12). Actual tests have shown that comparatively small changes in draw have produced a 30% change in tensile strength of the paper (5).

The paper is dried on a series of dryer rolls arranged in three sections of 20, 13, and 11 rolls, respectively. The sheet of paper passes around each roll in succession, being held in close contact by a heavy dryer felt or canvas (0.25 inch thick, cotton) which is sufficiently porous to allow ready escape of water vapor. The felt in the first section is dried by four separate dryer rolls; there are two in the second section. These are identical to those used to dry the paper sheet (Table III).

A pair of rolls, usually functioning as a secondary smoothing press but termed a marking press at Camas, is located between

the first and second dryer sections. Small spring rolls maintain constant draw on the paper. A size press is positioned between the second and third dryer sections. The two rolls are equipped with a pan and shower arrangement for the application of suitable sizing materials to the sheet surface. The marking or secondary smoothing press and the size press are used to provide additional finish or caliper control (sheet thickness).

After leaving the last dryer section, the sheet of paper is essentially dry, averaging 5 to 6% moisture. Finish is applied to the paper by passing it through a series of chilled iron calender rolls. Only the bottom roll is driven so that there is some slippage between adjacent rolls, producing an "ironing" action on the sheet. Some of the rolls are drilled for water or steam. The sheet is passed back and forth starting at the top of the stack. The desired paper finish is obtained by varying the number of roll nips; by auxiliary pneumatic loading; and by circulating water or steam through the calender rolls.

After passing through the second calender stack, the sheet is wound on a steel reel spool. When the roll attains the desired diameter, the paper coming off the machine is transferred to an empty reel spool. The full one is removed to the machine winder by means of an electric hoist. The paper is rewound usually on paper cores and at the same time it is slit to the desired roll length, the deckle edge is trimmed, defects removed, and splices made. The paper is ready for shipment in rolls or it is sheeted according to the specific demands of the customer. At Camas much of the paper is converted to bags, wraps, and other consumer shapes in another part of the mill. Paper is wrapped, stenciled, and made ready for delivery to railroad boxcars.

WHITE WATER AND BROKE RECOVERY

Since a large percentage of the fiber run onto the machine wire passes through and would be lost, the effluent must be conserved.

The white water passing through the wire at the table rolls and flat-box section carries about 10 pounds of fine fibers per 1000 gallons. This dilute suspension is collected in the wire pit directly beneath the Fourdrinier. About 90% of the white water is returned to the fan pump to dilute the fresh stock entering the head box. The remainder passes into a tile-lined white-water chest (5000 cubic feet) from which it is pumped to a disk filter (23E).

About 90% of the fines are removed and returned as wet filter cake to the machine chest. A portion of the raw stock from this chest is mixed with white water just ahead of the filter. This is known as "sweetener stock" and provides the heavier mat on the filter wires for more efficient recovery of fines. As much filtrate as needed is pumped to be used on the paper

TABLE V. CONTROL DATA

Paper grade Kraft pulp	Bag Unbleached	Waxing Semibleached	Tabulating card Semibleached	Wet strength specialties Semibleached	Meat wrap Semibleached	Wrap and bag Fully bleached
Pulp brightness, % on G.E. instrument	..	30	65-67	65-67	65-67	80
Basis weight range, lb./ream of 500 24 X 36 inch sheets	30-60	40	101	45-55	42-52	35-50
DEFINITIVE PAPER TESTS (16E, 17E, 30E, 35E-39E)						
Bursting strength, lb./sq. inch/ unit basis wt. X 100	81+	91+	70+	95+	64+	53+
Aggregate tear, Elmendorf units/ basis weight	4.0+	3.5+	4.0+	..
Ink, min.	30+	..
Size, sec./basis wt.	1.8	..	1-1.2	..
Caliper or thickness, inch	0.0067
Stiffness, Taber units	18.0+ with machine direction; with cross machine direction	8.5+ 10+
Wet tensile strength, lb./0.5- inch strip/basis wt. X 100 (with machine direction)
Air permeability, seconds re- quired for 100 cc. air to pass through 1 sq. inch	..	50

FOURDRINIER PAPER MACHINE

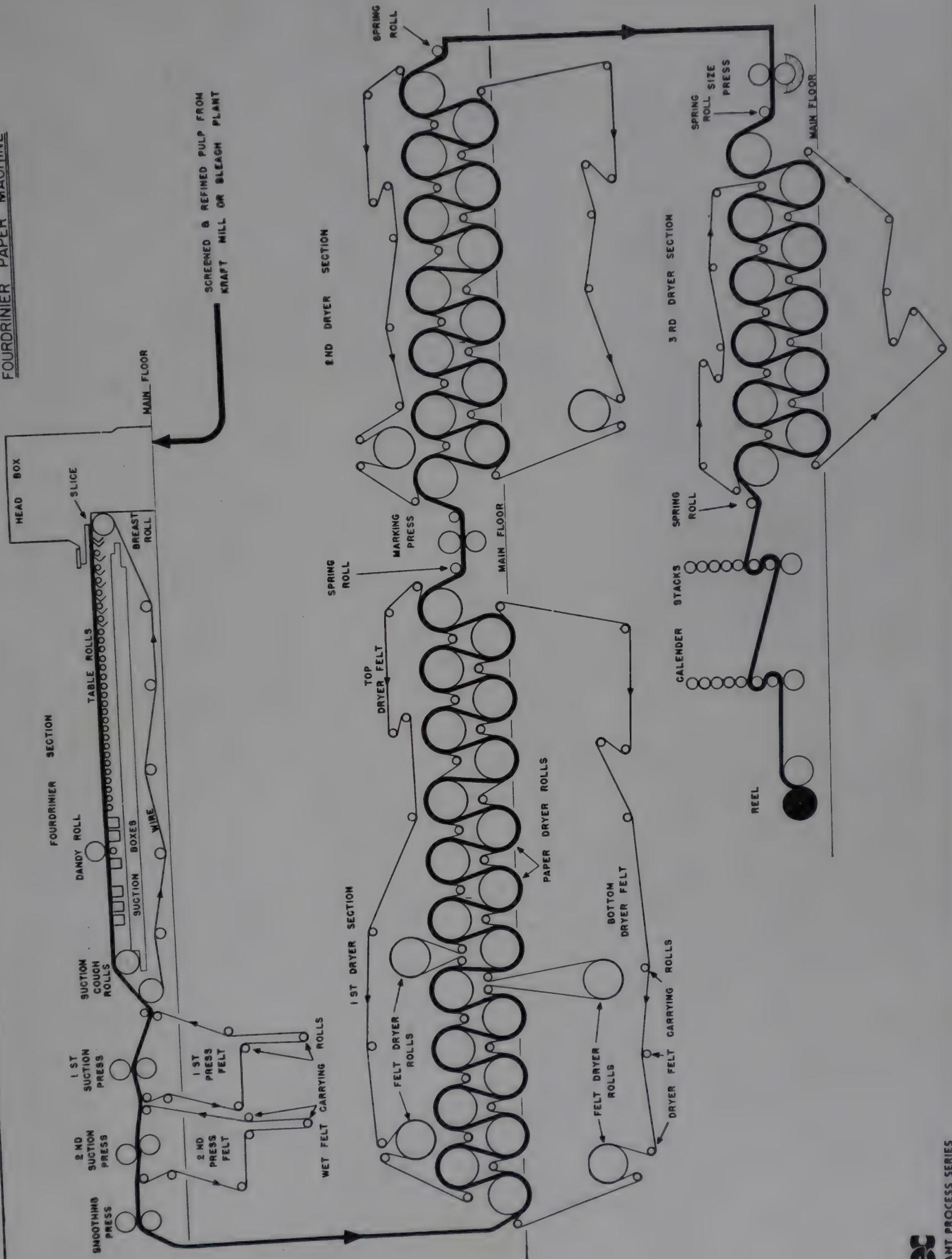
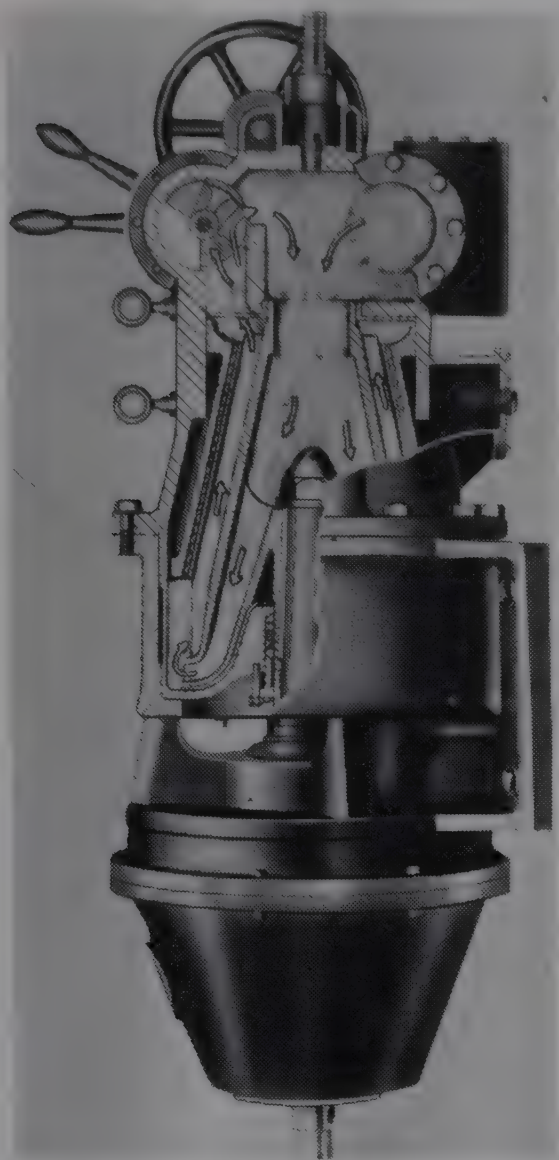


Figure 10. No. 15 Fourdrinier Paper Machine at Camas Mill

machine as dilution water in the stock regulator, head box showers, or showers on the rolls in the Fourdrinier section. Filtrate not used for these purposes overflows a weir to the sewer.



Cross Section of Morden Stock-Maker

Facilities must be provided for handling "broke" or paper that has been discarded anywhere in the process of manufacture. This may accumulate during breaks on the paper machines; as trim or defective paper removed at the winder; or as off-quality paper made during changes. In the basement approximately underneath the machine winder is a broke beater which repulps all dry broke accumulated. After being thoroughly pulped in the broke beater, the stock is returned to the secondary beater chest.

If paper breaks on the machine, the sheet either drops off the last couch roll into the wire pit or is doctored off the first press roll while the tail consisting of a narrow width of sheet is taken through the dryer section. The sheet coming off the wire is mixed with the stock entering the white-water chest. The sheet doctored off the first press roll is known as wet broke and is repulped in the broke beater.

During changes of paper grade on the machine, surplus stock drops into the white-water chest, then it is pumped to a tile-lined reclaim chest (1400 cubic feet). Stock from the broke beater, white water which cannot be used back in the system, and stock from the filter vat can be sent to this chest. From here the stock is pumped via a float control valve to the mill's central reclaim system where it is used to make lower grade papers.

To ensure cleanliness of product, as well as maximum equipment life, great care was taken to select materials of construction which would resist corrosion and have no tendency to stain or discolor the stock. As mentioned before, all chests are tile-lined. Stock and water lines are either of wood or transite. Machine and equipment parts are of stainless steel or other special alloy, or micarta, or are rubber-covered.

MOISTURE CONTROL

To ensure proper moisture control of the sheet on the paper machines, the paper and felt dryer rolls are divided into five sections. The first eight dryers of the first section comprise the first control section. The remainder of the first section, together with the second and third dryer sections comprise the second, third, and fourth dryer control sections, respectively. The six felt dryer rolls are controlled independently to form the fifth control section.

Moisture-laden air must be removed immediately from the vicinity of the sheet within the dryers. This is done by a series of five 2-speed exhaust fans (33E) which draw the air from around the dryers and blow it out the stacks. Moisture-laden air is prevented from collecting in pockets within the dryer sections along the length of the machine. The air is provided by a separate fan and is heated by exchange with steam (34E).

Four heating and ventilating units provide a continuous supply of warm air in the upper part of the machine room. This, together with the air provided through the nozzles, provides fresh air to the dryer section.

In addition to the moisture control afforded in the four dryer sections, the final sheet moisture and finish can be regulated, if necessary, by sweating the final dryer and spring rolls. Sweat is caused by passing cold water through these rolls. Water may be added directly to the surface of the sheet on the first calender stack by means of a water box for finish or caliper control. Each calender stack roll is fitted with a hollow center which can pass either water or steam. Under normal operation, if used at all, water is run through the first stack rolls and steam in the second. The production from the paper machine is largely dependent on the amount of drying possible.

INSTRUMENTATION

The philosophy which guides the instrumentation on the No. 15 Fourdrinier machine is simple and practical. In the first place, the operator must know what the instrument does, how it operates, and how it affects his product. In the second place, for maximum effectiveness the instruments and control levers must be easily accessible; should be in sight of the control point; and should be in a natural location regarding the process.

It is necessary to control the pH at the stuff box in order to set the sizing agents and to control drainage of water through the stock on the wire. Alum is added at the stuff box and the pH is measured (22E) at the exit side of the fan pump. This represents a time lag of 5 to 7 seconds. It is necessary to have proportionate control and reset (6E, 10E). Instead of open and shut valve control on the alum line, the valve opening is directly proportional to the pH reading above a set value ranging from 4.5 to 6.0, depending on the stock.

At the running speed of the No. 15 Fourdrinier, the level of stock in the head box could not be read accurately with a sight glass. A bubble-type system dispenses with the sight glass and also records any level changes.

The vacuum in the suction boxes must be controlled accurately because of the large suction area and, more important, because of the danger of wire breakage during a slowdown. In this case, pulp would pile up over the suction boxes; wire wear would be excessive; with the end result that the stock might be pulled into the boxes with wire rupture (freezing of the wire). A straight proportional controller adjusts the vacuum by operating a by-pass valve around the vacuum pump. This enables the flat box suction to be adjusted up to the capacity of the pump.

On the primary and secondary couch rolls, the vacuum is recorded, and the power to drive the helper motors is controlled (11E) by the vacuum carried at those points. This permits a more constant load on the belt drive and allows better control of the draw off the couch.

CONTROL DATA



Figure 11. Paper Test Station

Instruments, left to right: fold tester, stiffness gage, burst tester, tensile tester, glarimeter, densimeter, and opacimeter

Press rolls are loaded pneumatically. The air pressure in diaphragm cells is regulated by valves located in the pedestals supporting each press section. Front and back trunnions are loaded separately. An instrument (12E) records the loadings for each press section. The same type control is applied to the smoothing press and size press.

For control purposes, the paper and felt dryer rolls are divided into five sections. The temperature in each of these is controlled by a resistance thermometer instrument (13E). The five controllers are grouped on a central panel for convenience of the operator. If desired, the highest temperature may be maintained in the first section of eight dryer rolls in order to set the size in the paper. Each dryer section has its own condensate removal system (20E). Thermal compressors circulate steam through the rolls and remove condensate. Siphons revolve within the paper and felt dryer rolls to remove condensate which tends to follow the inner periphery as the speed approaches 1500 feet per minute.

The speed of paper through the last dryer section is measured by a tachometer (5E). This is connected with an alarm (15E) which warns of any sheet breakage. Total consumption and dryer usage of steam are recorded by separate flowmeters (32E). All steam is delivered from a 150-pound-per-square inch system, then reduced to 100 pounds per square inch at the paper machine before passing to the header supplying the dryer sections.

The Fourdrinier machine is driven by a line shaft connected to a single direct current drive motor whose speed is varied by both armature and field control. The line shaft is connected to all sections of the Fourdrinier through reduction gears, belts, and cone pulleys. The wire is driven by the couch rolls. The main couch is coupled with the line shaft and also to a helper motor (100 hp., direct current, 1150 r.p.m. through 6-1 gear reducer). The electrical system for the No. 15 Fourdrinier is shown in Table IV. The primary couch is driven by a helper motor only (60 hp., direct current, 1750 r.p.m. through 6-1 gear reducer). The helper motors apply power directly to these rolls depending on the suction being carried. The heavier or denser the sheet, the greater will be the suction. This in turn actuates an instrument which positions a rheostat in the electrical circuit of the couch rolls to increase the power input to the helper motors. In this way, the greater the load on the wire, the more power available to drive it.

The properties of several different grades of paper made on the No. 15 Fourdrinier machine are shown in Table V. These typical grades are made from unbleached, semibleached, and fully bleached kraft and represent a range of uses from ordinary wrapping and bag paper to highly specialized sheets.

The details of manufacture, including furnish, paper machine settings, and paper specifications, reflect the uses to which the sheet will be subjected. For instance, meat wrap is a hard sized sheet to resist penetration of moisture and meat juices. This wrap requires a large amount of size and a considerable amount of alum to set the size. The proper quality of sheet is assured by adequate specifications both for size test and ink penetration (8E).

A semibleached kraft waxing sheet requires a normal amount of size and alum, but the stock must be refined in such a manner that the wax absorption and penetration are not excessive.

To obtain a degree of wet strength, which is required in a number of specialties, melamine-formaldehyde resin is added at the machine stuff box. Note that this is the only item shown in Table V on which a wet tensile test is indicated.

Whatever the grade, strict adherence to the customer's requirements is ensured by quality control involving the essential paper tests such as burst (mullen), sizing, caliper, stiffness, and moisture (Figure 10) (8E, 16E, 17E, 30E, 35E-39E).

FUTURE

All trends indicate that as the population of the United States increases, the per capita consumption of paper and paper products increases at an accelerated rate. Perhaps the biggest improvement in the papermaking process will be due to the application of new chemicals. Synthetic resins, synthetic rubbers, new coating compounds, more effective slime control agents and many other specialties will all make for improved papers (22) in the future. Of course, some aspects of the age-old problem of sizing remain unsolved. With modifications in rosin and wax sizes, perhaps the day will come when every paper mill in the nation will look back on the dark years when sizing presented operating and specification headaches.

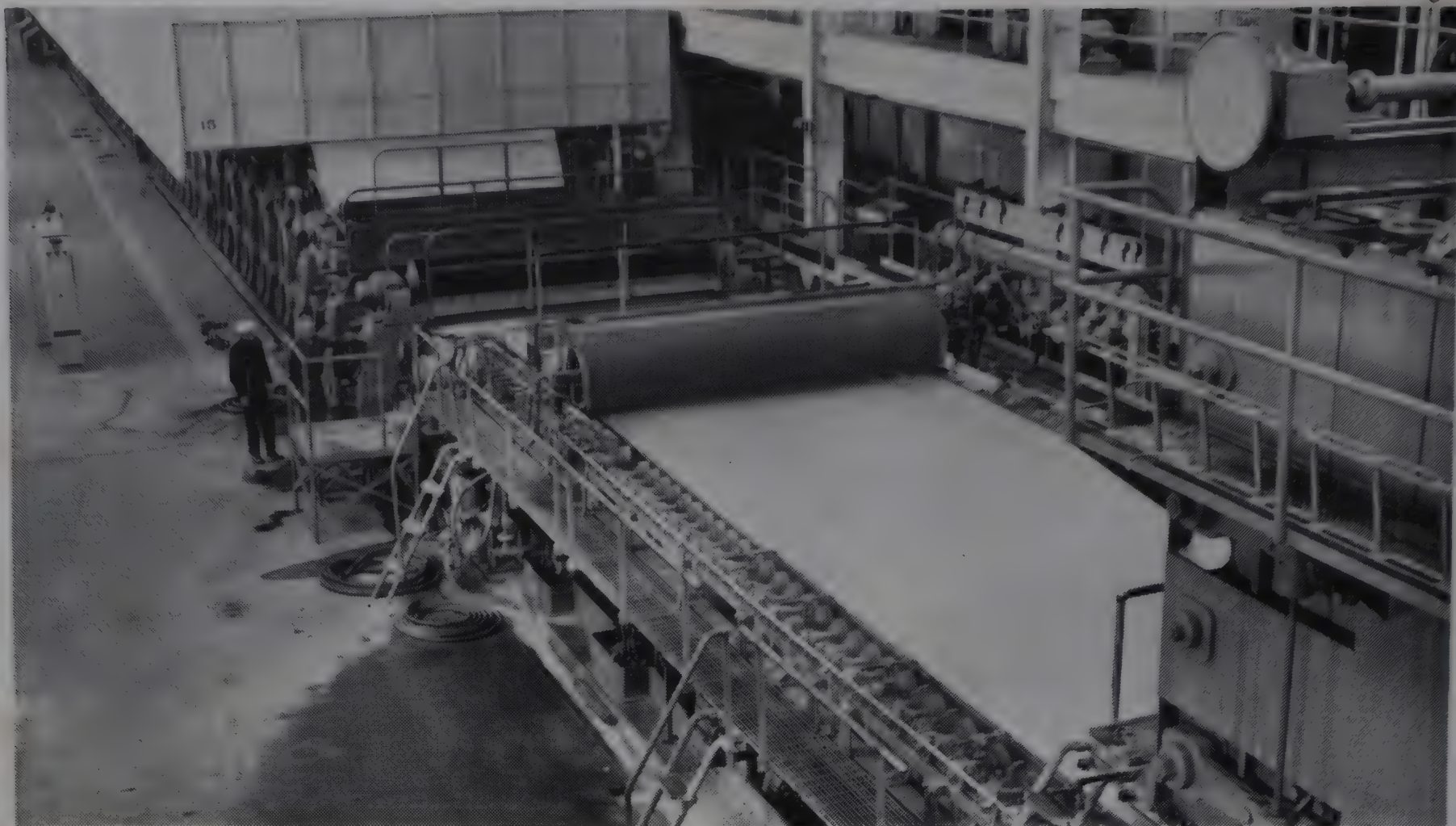
Just how far paper products will go in their displacement of other materials, such as metals, fabrics, and glass, is difficult to say, but many of the advances in manufacturing techniques, resulting from the stringent requirements of World War II, will be improved still further.

ACKNOWLEDGMENT

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Slab of Finished Stock is Cut from Wind-Up Roll of Refiner at Midwest Rubber Reclaiming Co., East St. Louis, Ill.

RODNEY N. HADER

Associate Editor

in collaboration with

D. S. LE BEAU

Midwest Rubber Reclaiming Co., East St. Louis, Ill.

MANY of the thousands of rubber products manufactured in the United States today owe at least part of their properties to an unsung, glamourless constituent, reclaimed rubber. Reclaim, as a commodity, has enjoyed a steadily increasing market throughout the last century (Figure 1). When we were deprived of sources of natural rubber during World War II, reclaimed rubber bridged the gap in the supply of rubber hydrocarbon and maintained the flow of transportation. Today the productive capacity of this country's reclaiming industry, on the basis of a 6-day work week, 24 hours per day, amounts to about 355,000 long tons per year.

In the latter half of 1950, when prices of new rubber began an uneven and possibly unwarranted upward climb, and the Federal Government ordered curtailments in raw rubber usage and increases in government stockpiling, the reclaiming industry was sufficiently adaptable to absorb some of the shock of the situation. For example, the Midwest Rubber Reclaiming Co., whose standard schedule is a 5-day week of 24-hour operation, expanded almost at once to 24-hour, 7-day operation and

established new production records in both its Barberton, Ohio, and East St. Louis, Ill., plants.

The event that provided the first great stimulus to the use of "gum elastic" was the same that set the stage for rubber reclaiming. In 1839, Goodyear discovered that the properties of natural rubber could be improved vastly by the incorporation of sulfur, and almost immediately there was rapid expansion in the manufacture of rubber products to satisfy the pent-up demand for practical rubber goods (2). Consumer demand for the new, improved articles became so great that normal raw rubber supplies were not sufficient to keep pace with production, and the need for a secondary source of supply became urgent. By about 1850, it was apparent that the reclaiming of scrap rubber was the most practical means of filling this need.

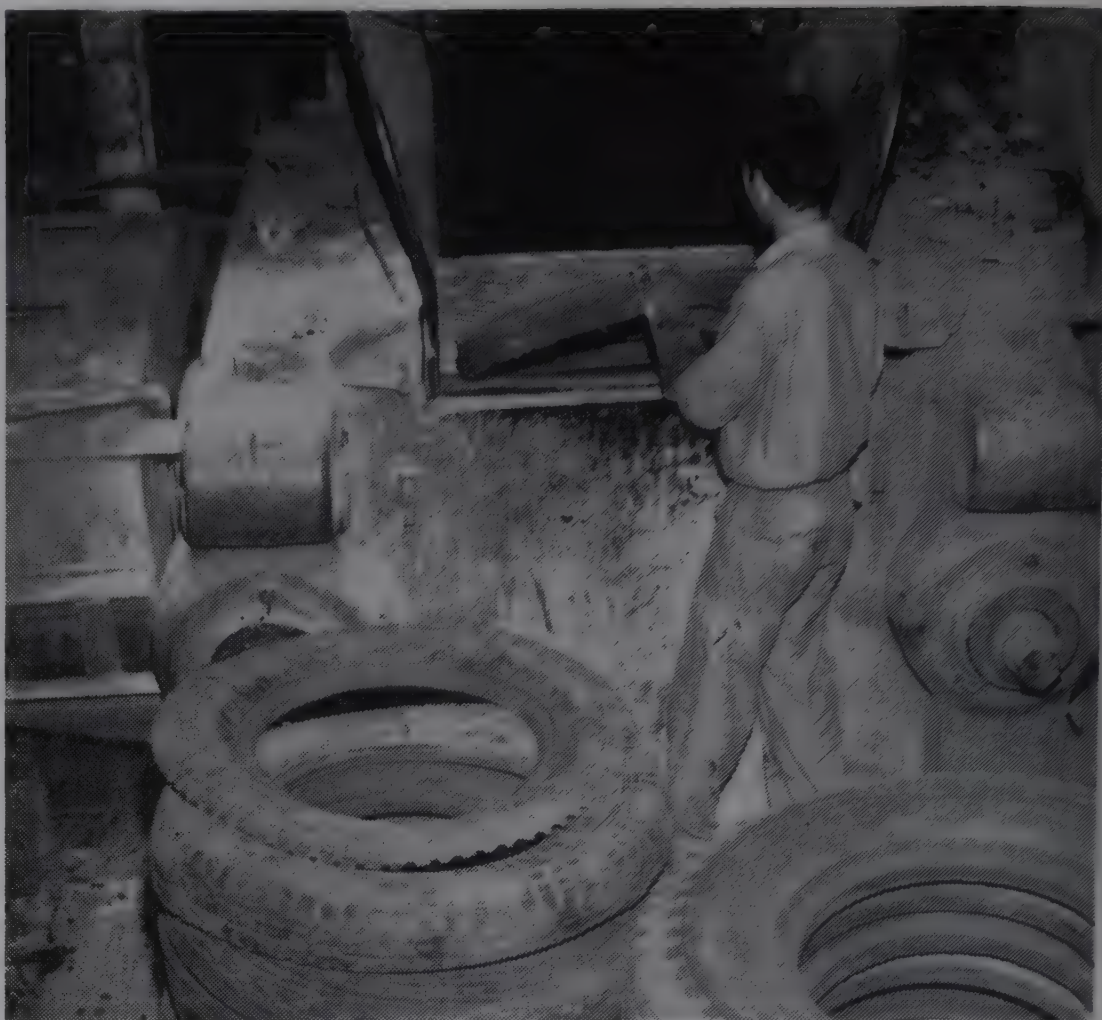
CHEMISTRY OF RECLAIMING RUBBER

The term devulcanization has been used indiscriminately to describe many reclaiming processes. Originally vulcanization

was the term applied to the changes brought about in rubber by the chemical addition of sulfur. However, by the converse of this definition, the reclaiming of vulcanized rubber should not be called devulcanization; it has repeatedly been shown that, regardless of the process, the removal of sulfur combined by primary valence forces is not achieved (10).

Within the last decade, vulcanization procedures have changed radically. The introduction of organic accelerators greatly reduced the amount of combined sulfur required in vulcanizates. Polychloroprene was found to be vulcanizable by the addition of metallic oxides without any sulfur. The present-day concept of vulcanization is primarily one of polymerization of the elastomer, brought about by both chemical and physical forces within and between molecules. In accordance with this concept, "devulcanization," as applied to the reclaiming of natural and synthetic rubbers, is properly defined as depolymerization. Uncombined sulfur is dissolved from the rubber mass by some reclaiming methods, but this is entirely independent of the reclaiming reaction. Reclaiming is strictly a matter of molecular breakdown.

The chemistry of rubber reclaiming may be considered either very simple or very complex, depending on the viewpoint chosen. From the operator's standpoint, it is simple: for the most part, common, technical grade chemicals are used, and the reaction proceeds readily without the necessity for exact techniques. To fundamental chemists, however, the process is anything but simple, for the composition of the rubber scrap is highly complex at the start, and the products of fiber degradation are so numerous and so diversified in nature that analysis of the digester liquid is almost impossible. Although it is known that caustic soda hydrolyzes much of the cellulose in fiber-containing scrap to sodium carbonate, the role played by caustic in the reclaiming



Over-Sized Tires, Halved by Splitter, Are Fed to Cracker Rolls

process has never been fully understood, and it is doubtful whether all the reaction products have ever been identified, even in the days when scrap rubber was less complex. The reaction products obtained from the hydrolysis of cellulose with metal chlorides are equally varied and no less complex.

Scrap from articles manufactured years ago contained no carbon black, no vulcanization accelerators, and no antioxidants; only natural rubber was used, and the reclaiming process was simple. The development of organic accelerators tightened vulcanization and improved the properties of rubber for many uses but contributed difficulties to the reclaiming processes. The development and widespread use of reinforcing carbon blacks and other fillers added to the problem by introducing strong secondary forces. Finally, the introduction of synthetic polymers and the alterations produced in the reclaiming processes by reactions specific to the molecular structure and configuration of the synthetics further complicated operations.

Synthetics

The decision to produce GR-S in large amounts as an all-purpose rubber accelerated efforts toward the development of satisfactory methods for its reclamation. As the art of tire compounding progressed, natural rubber and GR-S were used together or interchangeably, and methods for the satisfactory reclaiming of mixtures of the two rubbers had to be established. Inasmuch as GR-S, Butyl, and natural rubber are the three polymers produced and used in the largest quantities in this country they make up the greatest proportion of the scrap available to the reclaiming industry. The amount of scrap available from Hycar and neoprene is comparatively small. However, these two polymers as well as Butyl are now reclaimed with equal success

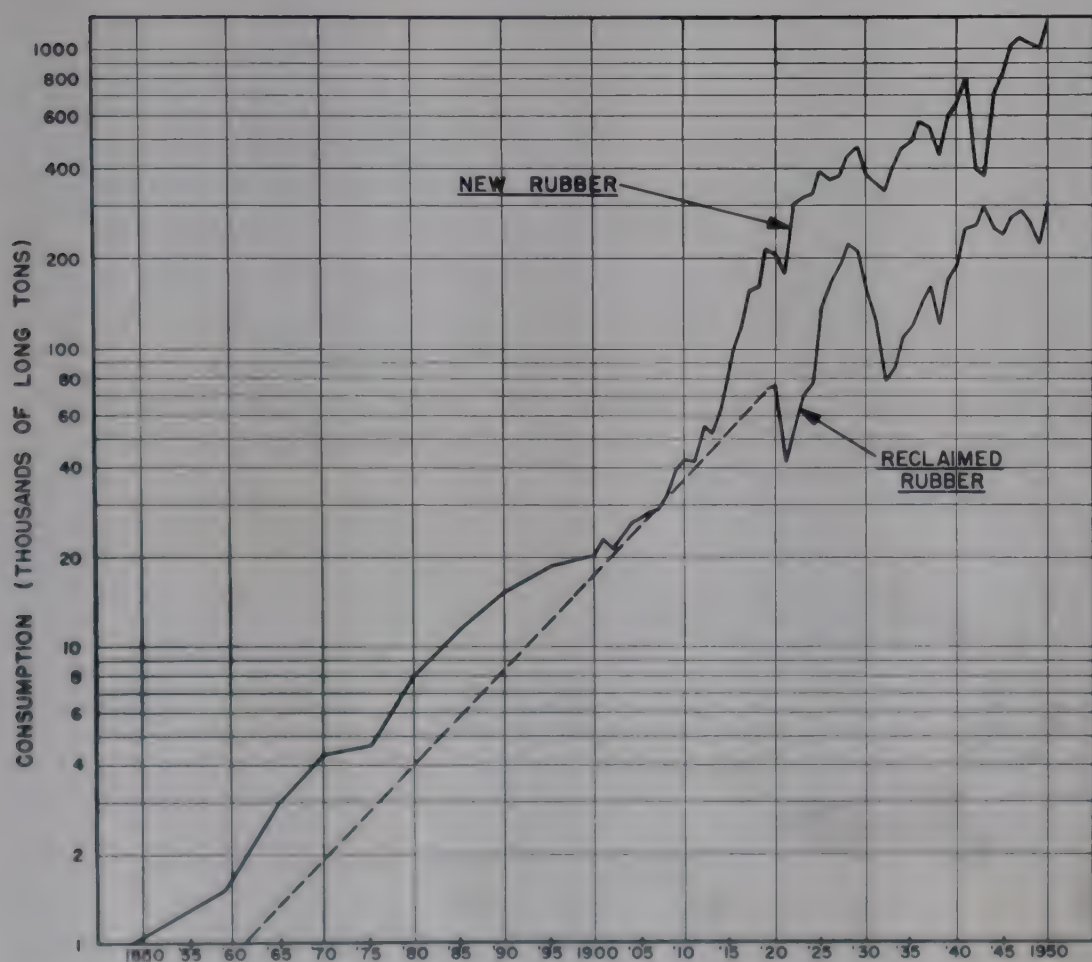


Figure 1. Consumption of New and Reclaimed Rubber—1850-1950



Sealing Digester Preparatory to Admission of Steam to Jacket

by conventional methods, with the judicious use of appropriate reclaiming agents.

The breakdown of olefin polymers in reclaiming has been definitely linked to the presence of oxygen in the reaction system (14, 21, 24). The formation of active radicals, caused by the application of thermal energy in the presence of traces of oxygen, can be considered the first step in the process leading to hydroperoxidation of the unsaturated hydrocarbon chain (5, 6, 11, 15-17). The location of the peroxide formation within the hydrocarbon polymer molecule is determined by the alkyl substitution in the chain; in natural rubber it will occur at the α -methyl carbon (15) and not at the double bond.

The olefin hydroperoxides are highly unstable compounds, and their breakdown accounts for the depolymerization of the rubber hydrocarbon chain. Strong support is given to this hypothesis by the fact that very little if any decrease in the total unsaturation of natural rubber is effected during the reclaiming process. Furthermore, infrared spectrography (9) has shown that reclaiming does not cause an increase in the amount of combined oxygen in the hydrocarbon molecule over and above the traces of oxygen present after compounding and vulcanization but prior to reclaiming. Finally, the presence of alkali or metal chloride used to destroy the fiber was found to affect the rate of breakdown during the reclaiming process (8). This is in agreement with the findings of other investigators (15), who showed that the acidity or alkalinity of the medium affected the breakdown reaction of olefinic materials.

The position of double bonds in an olefinic polymer has a strong influence on the course of the reclaiming reaction; linear polymers having terminal double bonds in the side chain (synthetic elastomers) will not react in the same way under identical reclaiming conditions as will polymers which have double bonds in the main chain only (natural rubber). Infrared spectrography has shown (1, 18) that GR-S consists of a number of possible molecular configurations inherent in the polymerization behavior of the mixed monomers, as well as in the behavior of incipient copolymers that result. Consequently, any molecular breakdown of GR-S will be a function of its complicated configuration and cannot be delineated as straightforwardly as the breakdown of natural rubber.

The reclaiming process causes the predominant scission of the natural rubber hydrocarbon molecule, followed by a smaller amount of recombination of chain fragments as the time of reclaiming progresses. The net result is a considerable increase in plasticity. However, the structure of GR-S causes at first a considerable amount of scission of its molecules which, as the time of reclaiming proceeds, is soon overshadowed by extensive recombination of molecular fragments (7, 22, 31), resulting in a progressive and extraordinary hardening of this polymer during the reclaiming process (Figure 2). The rates of scission and recombination of chain fragments of both polymers are affected by the presence of defibering agents and by the temperature at which the reaction is carried out.

Inasmuch as it is practically and economically impossible to segregate the natural rubber hydrocarbon from its synthetic partner, this difference in the behavior of natural and synthetic rubber hydrocarbon has caused numerous difficulties during the reclaiming process. To obtain devulcanized stock of an all-over uniform plasticity it is possible either to interrupt reclaiming after a short time (7, 22, 30) and make use of the extraordinary increase in plasticity while scission predominates in the

GR-S, or to continue reclaiming, using reclaiming agents which will prevent the heat hardening of the GR-S. Advantages may be claimed for both methods.

Reclaiming Agents

The chemical groups in general use as reclaiming agents today are alkylated phenol sulfides, aromatic mercaptans, amino compounds, and certain unsaturated compounds present in coke oven by-products. The reactions which make these compounds useful are not fully known. Substitutional groups may exert a considerable influence on the reclaiming activity of a compound, while isomeric differences in the molecular structure account for only minor differences. This was found to hold true for the alkylated

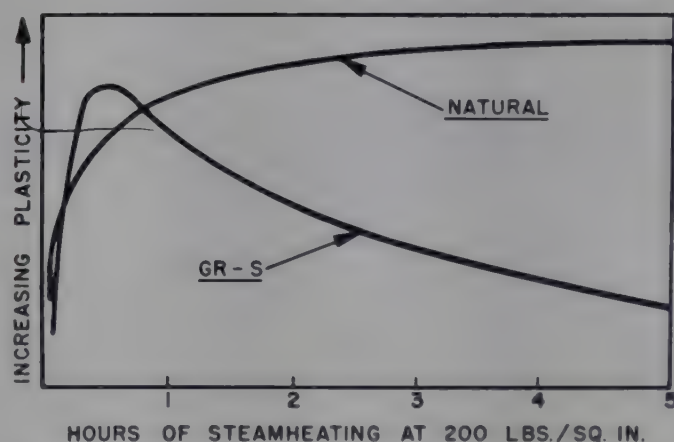


Figure 2. Plasticity of GR-S and Natural Rubber during Reclaiming Process

phenol sulfides (11). The reclaiming reactions of the compounds present in coke oven by-products, on the other hand, were found to be connected with their hydroperoxidic activity, and the position of a substitutional group definitely influenced the reclaiming activity of the compound (10). The reason for the retardation of the recombination of molecular chain fragments (heat hardening) of GR-S polymer, which is most pronounced when amino compounds are used, is not yet known.

Most of the reclaiming difficulties arising from the structures of neoprene and Hycar are similar to those encountered with GR-S.

Heat hardening is extraordinarily pronounced for vulcanized neoprene and Hycar, and reclaiming agents which retard the recombination of molecular fragments are naturally more effective than others.

RECLAIMING PROCESSES

The history of the rubber reclaiming industry has been one of relatively frequent major revisions, keyed to changes in the rubber goods manufacturing industry which provides reclaimers with their only source of direct raw materials. Hence, in addition to normal technological advancements, radical changes have been necessitated at several periods because of the shifting of emphasis in the manufacture of new rubber articles.

Early solid rubber articles, such as car springs—a variety of molded shock absorbers used as mountings in horse-cars—gave way to fabric-containing, lightly vulcanized rubber footwear; this became the first large-volume source of scrap rubber for reclaim and provided the major source from 1860 until about 1915.

Toward the end of the nineteenth century, the bicycle industry developed a thriving activity because of the introduction of the pneumatic rubber tire in 1889. Bicycle tire production reached its peak in the United States from 1892 to 1894; this resulted in heavy demands on the reclaiming industry for its product and provided, in turn, a large supply of scrap rubber in a new form.

From about 1890 to 1910, solid rubber tires for carriages and buggies and later for automotive trucks also provided an important source of scrap rubber. Eventually, solid tires for automobiles and trucks were replaced by pneumatic tires, and today these provide at least 85% of all scrap rubber reclaimed.

Goodyear himself was among the first to perceive the desirability of recovering rubber for re-use, and in 1853 secured one of

the earliest patents in the field (19). His process was a purely mechanical one, involving a grinding operation to reduce the vulcanized rubber to a finely divided state and then mastication to mix the reclaim with raw rubber. This process was successful because of the low degree of vulcanization of the rubber articles of that time and because of the lack of reinforcing fillers.

Pan or Heater Process

A complete history of the development of various reclaiming processes has been compiled by Ball (2). The first significant step toward actual reclaiming was the development of a process which involved restoration of vulcanized natural rubber scrap through the application of heat. This process, which in principle is still used to some extent, was exploited by placing the finely divided scrap in shallow open pans and subjecting it for several hours to the direct action of steam or hot water in a closed vessel. Although the steam-treated waste never regained all the properties of raw rubber, it was at least partially devulcanized and was amenable to revulcanization and re-use. The product of this process, which was first patented in 1858 by Hall proved a much more versatile raw material than that obtained from the mechanical process and paved the way for more widespread use of reclaim in rubber goods manufacture.

Separation of Fibers

The earliest reclaiming processes were successful principally because there was sufficient fabric-free scrap to satisfy the entire demand for reclaim, and no problem of fiber removal or fiber destruction had been encountered. As the demand for reclaim increased, however, it became necessary to employ more and more fabric-containing items—especially boots and shoes—in order that the growing demand might be met. The product was not

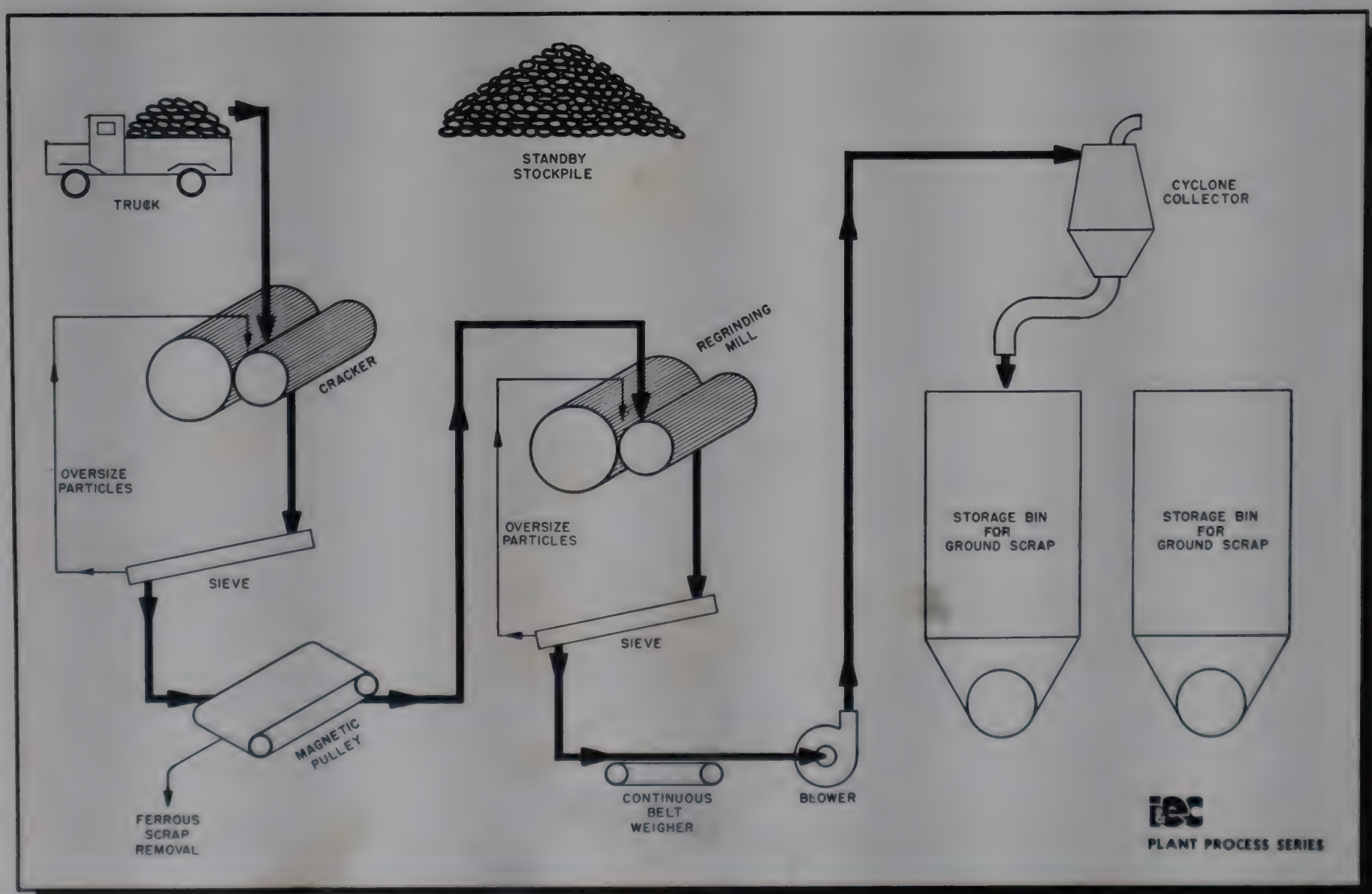


Figure 3. Flow Sheet for Preparation of Scrap Rubber for Reclaiming

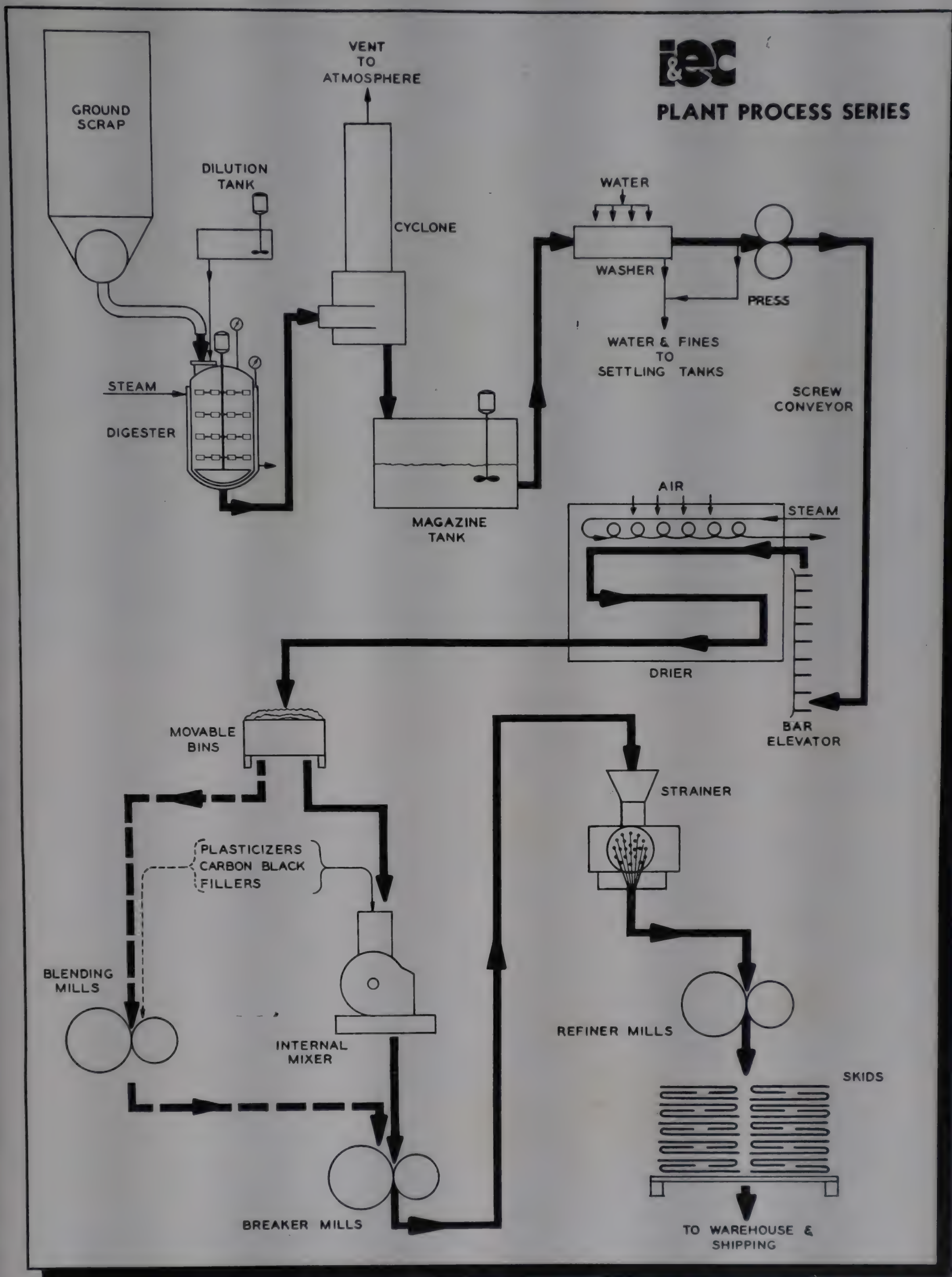


Figure 4. Flow Sheet of Digester Process for Reclaiming Rubber at East St. Louis, Ill., Plant of Midwest Rubber Reclaiming Co.



In the Heater Process Stock for Devulcanization Is Charged in Open Pans

of the highest quality; the development of methods for air separation of fibers from rubber scrap further improved the quality of footwear reclaim but it still remained mediocre.

Acid Process

Ground scrap was defibered in this process by the action of boiling sulfuric acid in lead-lined wooden tanks. The rubber was then given a water wash and was subsequently devulcanized by heating for 24 hours in closed vessels, using steam at about 300° F.

An important contribution to the reclaiming art at the time was the discovery by Mitchell (27) of the advantages to be gained by heating rubber wastes and fiber-destroying agents together in a pressurized vessel. Mitchell's improvement was of such importance that the use of the digester process or the omission of it soon became associated with the difference between first- and second-quality reclaim.

Alkali Process

The patent of 1899 which revealed details of the alkali digester process (25) has been described as probably the most important patent on the reclaiming of scrap rubber ever issued (2).

The significance of the alkali process lay in its simplification of reclaiming to a single-step operation. Any type of natural rubber scrap available could be simultaneously defibered, desulfurized, and devulcanized by a single heating with dilute caustic solution under pressure. Furthermore, the alkali process yielded a vastly superior product, with greater tensile strength and elongation, better working properties, and more "nerve"—the quality of natural rubber which gives it a high degree of resilience and causes it to recover its shape after distortion.

Neutral Process

In 1913, a patent was granted to Cutler (13) on the use of zinc chloride and pine oil to produce a neutral reclaim by the pan or heater process. The neutral process is widely used in digesters today to produce reclaims that are less tacky and less nery than comparable alkali reclaims, and less susceptible to prevulcanization during calendering or extruding operations.

The introduction during the last decade of high percentages of synthetic polymers caused great difficulties in the performance of the old alkali process. These difficulties were a direct function of the reactions of the synthetic polymers under the conditions of the process. As a consequence, the importance of the alkali process decreased and metal chloride defibering agents such as calcium chloride or zinc chloride were used to a much greater extent. Today fiber removal is accomplished either by air separation or by hydrolysis with a metal chloride or with alkali. Devulcanization may be achieved either simultaneously or in a subsequent operation.

Banbury Process

The decade between 1930 and 1940 saw the introduction of still another process, known today as the Banbury process. Ground vulcanized scrap is introduced into a Banbury mixer where in the presence of air it is worked under pressure and at high temperature for a very short time, either with or without a reclaiming oil (28). A subsequent patent (12) described a modification of the process, providing for mastication in the presence of controlled quantities of oxygen, air, or other autoxidation promoters and/or reclaiming agents. This modification recognizes the considerable strain placed on the Banbury machine by mastication of vulcanized scrap and attempts to minimize it by prior

steam heating of the scrap, thereby softening the rubber and reducing the strength of the fibers. Fillers such as carbon black may be added to help generate heat and friction.

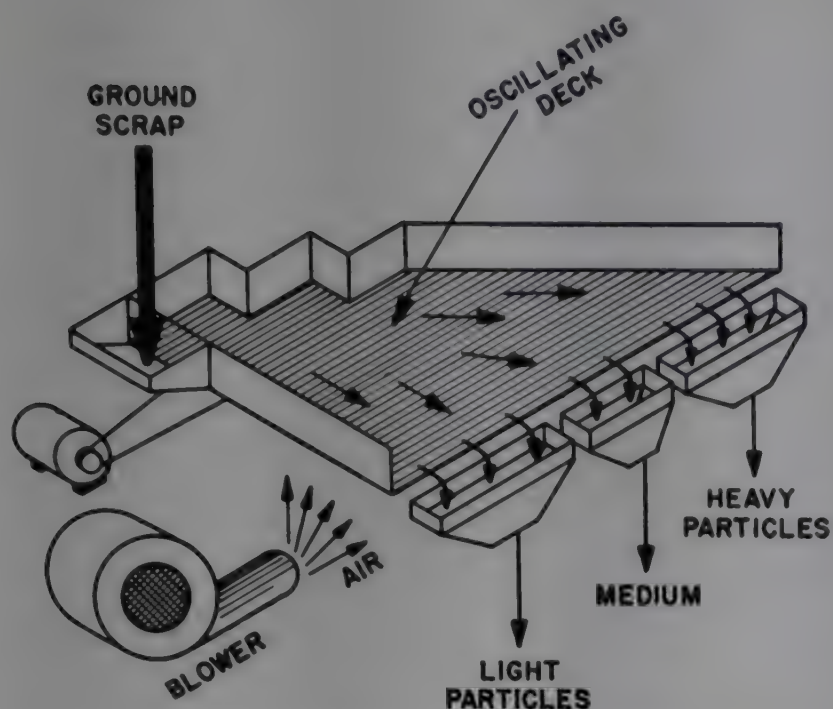


Figure 5. Grain Separator for Classifying Scrap Particles

In 1949 two additional patents were issued covering the re-plasticization of unvulcanized and scorched (partly vulcanized) scrap (4) and the reclaiming of vulcanized scrap (3). These processes also make use of mastication in a Banbury mixer, but the mechanical pressure under which the scrap is worked has been augmented to between 50 and 250 pounds per square inch; the speed of the rotors is two to three times that ordinarily used in this machine. The size of the motor used to drive the rotors must, of course, be considerably increased. After mastication the stock, which requires no washing or drying, is ready for refining. The Banbury process is used commercially for the reworking of unvulcanized and scorched factory scrap.

Screw Process

The Banbury process has not found any extensive use in the reclaiming of vulcanizates, but a modification of its principle using a screw-type plasticator has found commercial application. Very finely ground scrap, preferably defibered by air separation, is charged to the screw chamber along with reclaiming agents and fillers. Under the effects of pressure and heat the mixture is converted to a soft plastic mass which is cooled and extruded from the plasticator ready for refining by further working. Like the Banbury process this method exploits the extraordinary depolymerization of GR-S (Figure 2) during the early stages of reclaiming (30).

By far the largest amount of reclaim is still produced in autoclaves. The rates of both the chemical defibering process and the devulcanization reaction depend on the temperature at which the scrap is treated. In addition, the kind of cellulosic fiber as well as the kind of synthetic or natural vulcanized polymer present will influence the reaction.

EAST ST. LOUIS, ILL., PLANT OF MIDWEST RUBBER RECLAIMING CO.

The East St. Louis plant of the Midwest Rubber Reclaiming Co. was one of the first reclaiming factories designed to allow a straight-line flow of scrap rubber through the many steps from scrap storage to the final shipping dock. Midwest's plant operates smoothly and efficiently through careful scheduling and integration of a great variety of activities; it has a rated daily production of 85 long tons of reclaim.

Midwest was organized in 1928, with a new plant in East St. Louis, and operated as a subsidiary of the Akron Rubber Reclaiming Co., formed 5 years earlier with its factory at Barberton, Ohio. Through a consolidation in 1937, the two companies became one, and adopted the Midwest appellation for all subsequent operations. Through repeated expansions, the company has become one of this country's largest manufacturers of reclaim.

The flow sheets for the East St. Louis plant show the course of the major portion of the material handled. Small runs of special stocks or of materials destined for special end uses, may be handled according to other procedures, but by far the greatest portion of all scrap is processed as indicated by the flow sheets to make "whole-tire" reclaim (Figures 3 and 4).

For convenience and economy of operation, scrap vulcanized rubber, which is purchased on the market today like any other commodity, is fed whenever possible directly into the plant from trucks or boxcars, eliminating the multiple handling inherent in working from stockpiles. Large stockpiles are maintained and augmented or depleted in accordance with scrap shipments into the plant area, but their role is analogous to that of an auxiliary surge tank rather than an on-stream unit in continuous operation.

It is obviously economical to keep plant changeovers at a minimum: various feed stocks are scheduled as far ahead of plant operation as possible, therefore, in order to combine batches and attain virtually uninterrupted operation. The handling of automobile tire scrap, which comprises at least 85% of all scrap reclaimed, is best described as semicontinuous.

Preparation of Scrap

Whole automobile tires are fed into the "cracker," which is the first item of major processing equipment. Truck and bus tires, which are too large for direct feeding into the cracker rolls, are first halved on a semiautomatic splitter. This machine, which grips the tires and rotates them against the blade of a stationary knife, is one of the few machines developed specifically for the reclaiming industry.

The cracker is a horizontal roll mill with heavy corrugated rolls, having an exposed length of 38 inches between guides. At its speed of about 21 r.p.m., the larger roll, with a diameter of 28 inches, has a peripheral speed of about 156 feet per minute, and provides a friction ratio of 2.5:1 with the smaller roll, 20 inches in diameter. These rolls, set close together, afford both a cutting and a tearing action, and the scrap is rapidly reduced to pieces with a maximum dimension of a few inches. The mill rolls are water cooled to remove the friction-generated heat. Three crackers are used in parallel in the East St. Louis plant; all are mounted on a common shaft and driven by a 1000 hp. synchronous motor (6E).

The cracker discharges the shredded scrap onto a 36-inch belt conveyer, where an operator picks off the bead wires which have been stripped of their rubber by the action of the cracker rolls. It was once standard practice to debead all tires as a separate preliminary operation, but a saving in rubber and in operating costs is effected by combining this operation with the cracking step. Elimination of debearing made 94% of the average tire available for reclaiming instead of the 85% previously recovered.

From the belt conveyer, the scrap is discharged to a 5 × 10 foot oscillating sifter. Particles that are small enough to pass through the screen are carried forward to the next step in the process, and the coarse pieces are recycled to the same cracker for further subdivision. Depending on the type scrap being handled and the end use for which the reclaim is intended, the size of the screen openings used may vary from 1/8 × 2 inches to 3/8 × 7/8 inches. It is estimated that about 30% of the cracker discharge is recycled for further subdivision. Each cracker has a capacity of 5000 to 6000 pounds of suitably ground material per hour.

The 30-inch belt conveyer which carries the scrap from the

oscillating sifter passes close beneath a magnetic pulley, where an electromagnet removes ferrous tramp metal, such as nails and bits of wire picked up during tire service. The ferrous particles, attracted by the magnet, adhere to the moving belt interposed between the magnet and the moving scrap rubber below. The pulley belt carries the metallic particles beyond the field of magnetic influence and deposits them in a receptacle which is periodically emptied by an operator. The rubber particles which

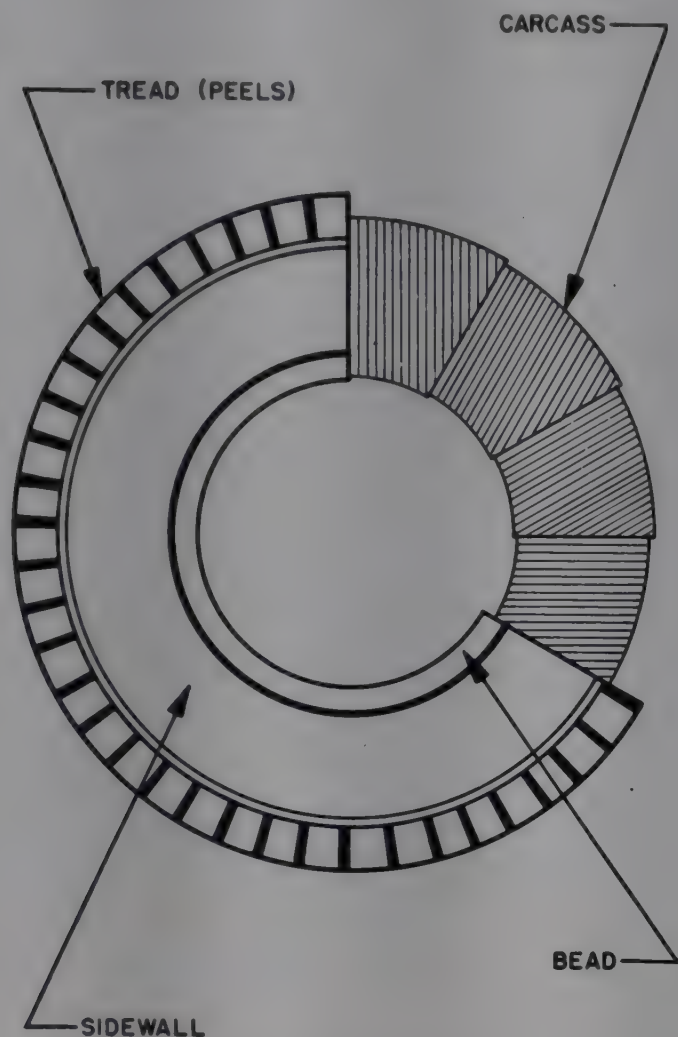


Figure 6. Tread and Carcass Segments of Tire Scrap Require Different Reclaiming Techniques

have passed through the sifter screen and beneath the magnet are transferred by air conveyor to a set of secondary cracker mills; these operate in a manner similar to that of the main crackers and grind the pieces of scrap into bits of a smaller and more uniform size. Like the crackers, the secondary mills are mounted on a common shaft, driven in this instance by a 450 hp. synchronous motor.

Four reciprocating screens (10E), each 40 × 84 inches, classify the product of the regrinding mills according to size; particles which will not pass through the screens and are therefore too large for proper penetration of reclaiming agents in subsequent steps are returned to the mills. Since particle shape, as well as size, influences the course of the digestion reaction and hence the properties of the final reclaim, slotted screens are employed to allow passage of rectangular particles.

The scrap particles which have passed through the screens are conveyed by air to a continuous automatic scale (4E) where an additional magnetic separation of metal is achieved by a magnetic head pulley. From this point the classified particles are transferred to large storage bins on the upper level of the building; the particles are blown along in a stream of air from which they are retrieved by cyclone collectors on the roof. The cyclones,

about 20 feet in height with a maximum diameter of about 10 feet, separate the rubber from the air stream and drop it into the bins below. The discharge ports of the bins are at a greater elevation than either the digesters or the open steam devulcanizer, allowing gravity feed from the bins to the processing units.

As a substitute for, or a complement to the reciprocating screens, a grain separator (Figure 5) can be used whenever desirable as a means of classifying scrap particles. This adapted apparatus separates fiber-containing particles from solid rubber particles, through differences in their buoyancy in a diffused air stream. The separation is accomplished on a porous deck, 12.5 feet long and 5.25 feet wide, which serves as a vibrating conveyor. A system of baffles beneath the deck permits delivery of a controlled volume of air from a centrifugal blower. Variable stock feed and the adjustable tilt of the table also help to control the separation. The mixed scrap is fed to the deck at one corner, and air rising through the material stratifies it according to its density. In the fluid mass, the heavy particles sink to the deck and are carried forward by its vibratory motion. The lighter, fiber-containing particles flow by gravity across the slightly tilted deck and are discharged separately. The particles of intermediate weight are recycled so that only two fractions are collected. The separation achieved is not perfect, but it is very helpful, since different reclaiming techniques may be required for the tread and carcass segments of the tire scrap (Figure 6). The fractions are recombined after digestion to yield whole reclaim stock, but they may be treated separately to attain the same final plasticity and yield a reclaim that is readily milled and uniform in properties.

Digester Process

The major portion of production at the East St. Louis plant is handled by a battery of 28 digesters, with batches charged and discharged on a staggered schedule to afford a continuous flow of devulcanized stock through subsequent departments. A normal charge consists of about 5000 pounds of scrap and about 10,000 pounds of dilute zinc chloride solution (ordinarily 1% or less in strength) or dilute alkali solution (approximately 4 to 6% in strength). The zinc chloride and caustic are purchased as 50% solutions and diluted in blending tanks as needed. The dilute solution of fiber-destroying chemicals is warmed to about 120° F. before it is added to the digester batch, and the reclaiming oils are blended into the solution during the warming process.

The digesters themselves are vertical jacketed autoclaves

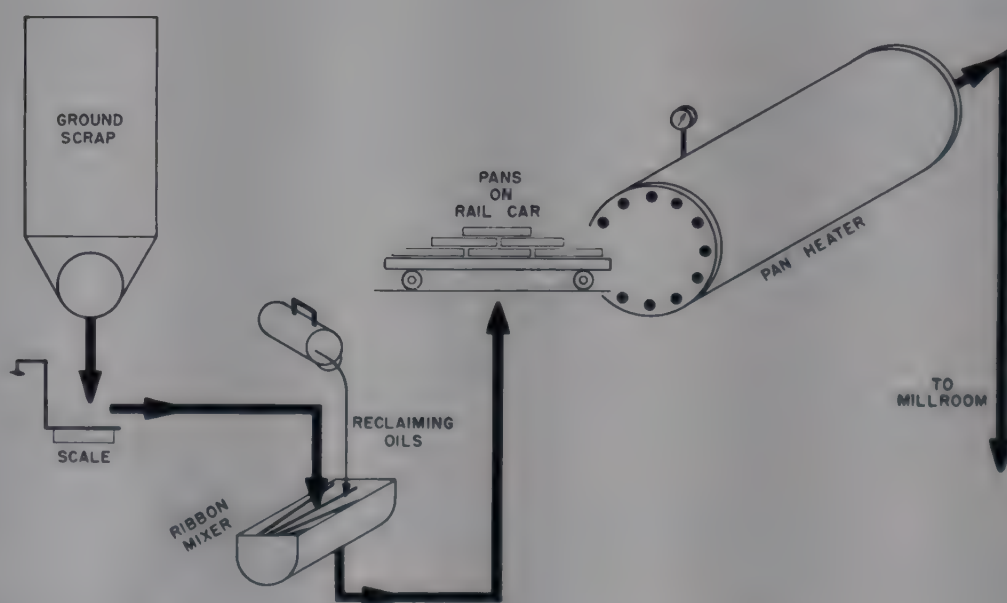


Figure 7. Flow Sheet of Heater Process

equipped with full-length agitator shafts. Each autoclave is 6 feet 3 inches in internal diameter and 10 feet high in the cylindrical



Devulcanized Particles after Washing and Dewatering Operation

Operator adjusts water flow to continuous washer

portion. Both top and bottom of the autoclaves are dished. Four sets of paddles are spaced along each agitator shaft, and an extra agitator conforming to the dished bottom prevents settling of the solids. Each agitator shaft is connected through a speed reducer to a 10-hp. motor. The agitators have a rotational speed of 12 r.p.m.

The digesters are rated for 250 pounds per square inch internal working pressure. When the charge has been admitted and the handhole is closed, steam is admitted to the jacket until the internal pressure in the digester is about 185 pounds per square inch. The internal pressure creeps above this level during the digestion cycle because some of the fiber decomposition products are gaseous. The amount of this increase in internal pressure will depend on the amount of fiber present and on the strength of the defibering solution. It has been observed only when metal chlorides are used as defibering agents. Carcass scraps, in which the fiber content constitutes a large part of the total batch (about 30 to 40%), can exhibit a pressure increase of as much as 75 to 100 pounds per square inch. A minor fraction of this increase can also be due to the use of reclaiming agents.

The amount and choice of reclaiming oils depend on the kind of scrap used. Tightly vulcanized or highly reinforced elastomer scrap usually requires greater amounts. Crude solvent naphtha obtained as a by-product from coke oven operations, dipentene, coal tars, and pine tar oil have been used for a long time and are still in use today. The introduction of synthetic rubber has caused the use of other chemicals previously described.

Petroleum solvent naphtha is not effective as a reclaiming agent, but it and many other solvents of appropriate boiling

point range can be used as diluting carriers for extraordinarily effective reclaiming agents, which are used in very small amounts only. The inert carriers have the effect of increasing the volume of the reclaiming agents, thereby permitting wetting and consequently contact of a greater part of the large surface of scrap particles with the oils. The result is a more uniform distribution of the highly effective reclaiming agents throughout the digester batch. These exceptionally effective reclaiming agents can be used in quantities as small as 0.25% by weight on the scrap, whereas less effective oils, as well as the inert carriers, may be used in amounts as high as 20% or more.

There is a natural limit to the usable amount of such compounds. Reclaim is evaluated on the basis of its rubber hydrocarbon (RHC) content. First-line tire reclaim contains an average of 50% RHC. If large amounts of ineffective reclaiming oils or inert carriers are added, the RHC of the finished product will be reduced. Since average vulcanized tire scrap, before reclaiming, contains approximately 58% RHC, any addition of reclaiming oils or other fillers must be made judiciously.

Washing and Drying. After 9 to 12 hours at elevated temperature and pressure, the digester batch is pressure discharged through the bottom port, and the now defibered, devulcanized stock is transferred to an 8000-gallon magazine tank about half filled with water for diluting the digester batch and washing the rubber free of soluble impurities. The blowdown of the digesters is accomplished through a cyclone, 8 feet in diameter in the section where the digester charge enters. The cyclone drops the solids into the wash tank and discharges steam and a small quantity of steam-distillable oils and fiber-decomposition products to the atmosphere through a tall stack 5 feet in diameter. Five cyclones and five magazine tanks are sufficient to accommodate the production of the digester department.

After preliminary washing in a magazine tank, the rubber is conveyed through a continuous washing machine where four sets of spray nozzles complete the removal of soluble residue. The charge is carried through the washers by a vibrating 20-mesh screen which allows the free passage of water but holds passage of fine rubber particles to a maximum of 1 to 2%. From the washer the wet devulcanized stock is transferred by screw conveyor to a wringer-type dewatering press (8E), where rollers press the stock against a perforated screen, reducing the water content to about 40%. Some stocks are more easily dewatered at this point by a squeezing action, and to provide for this alternative, each washer is additionally equipped with a screw-type press (2E). A digester batch of 5000 pounds can be washed and dewatered in 15 to 20 minutes.

From the dewatering operation, the stock is removed by screw conveyor to one of five continuous dryers (12E), each capable of handling 2500 pounds per hour. Each dryer is 8 feet wide, with an over-all length of 44 feet, including the feed hopper. The actual drying compartment in each case is 22.5 feet in length and is divided into six sections for air distribution. Rubber moves along on a wide endless screen through the dryer's three flights—top to center, to bottom, and out. Air is heated by steam coils at the top of the dryer, and passes downward through the rubber and the perforated belt. This seemingly upside down drying technique is used because of the great susceptibility of rubber polymers to heat. Under the present arrangement the air having the highest temperature contacts that part of the devulcanized rubber which is highly moist and therefore protected against oxidation. That part of the devulcanized rubber which contains the least moisture, and is therefore least protected against oxidation, is exposed only to the cooler air. The final moisture content of the discharged stock is held between 5 and 15%.

Some moisture is left in the stock intentionally, because it later assists in temperature control in the milling operations. Large amounts of heat are generated through friction in milling the reclaim, and the evaporation of the last traces of moisture in the stock helps to dissipate this heat and prevent damage to the

rubber. The rubber as discharged from the dryer is loaded in 1000-pound charges into movable bins, for transfer by hydraulic or electric hand trucks to the mill room. There the final compounding, blending, and masticating operations are performed.

Fines. The digester liquor, to which has been added the wash water, contains some rubber and decomposed fiber particles in the form of a fine suspension. For the dual purpose of saving the rubber and clarifying the plant's effluent water stream, these particles are recovered. The dilute suspension is pumped to a tank farm, where in a batch process the solids are allowed to settle out slowly, usually over a period of at least 6 hours, and the clear liquid is discarded. The sludge from the tanks is further concentrated to about 20 to 22% solids, in a continuous traction thickener (5E). The thickener is 30 feet in diameter and 7.5 feet deep at the outer edge. The sludge from the mechanical thickener is filtered by means of a continuous rotating 5×8 foot drum vacuum filter (9E) and dried on a drum dryer, 3.5×10 feet, designed to handle 1200 pounds per hour on a dry basis (3E). The resulting product is either packaged or transferred to the mill room, where it may be blended in as a filler for low priced reclaims.

Heater Process

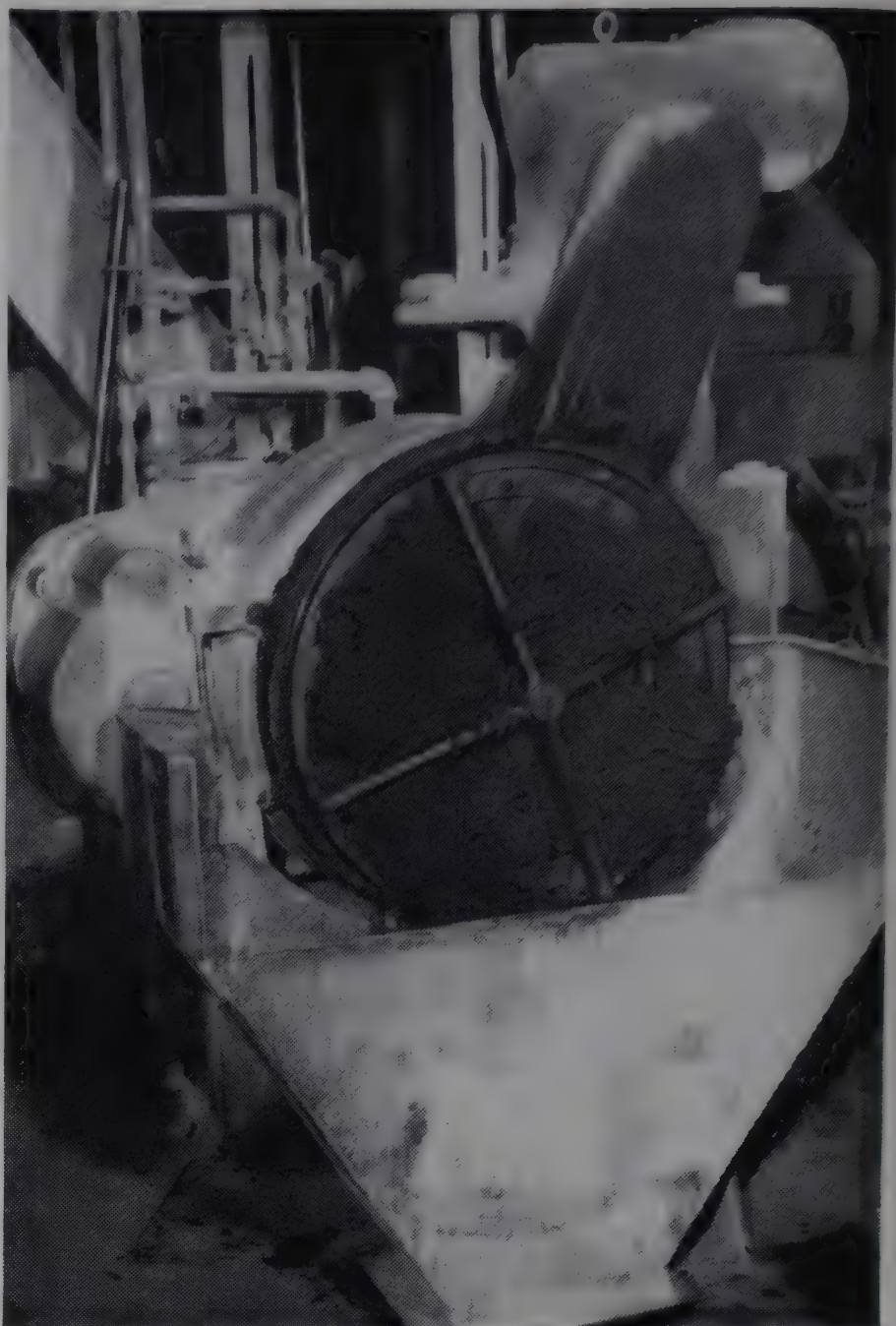
A small but significant portion of Midwest's production, approximately 10 to 15%, is handled through the open steam process (Figure 7) which produces a reclaim more suitable for some applications—inner tubes, for example—than the product of alkali digestion. The principal end use of heater process reclaim is in mechanical goods.

Finely ground scrap is weighed in small lots of 100 to 200 pounds and intimately blended with reclaiming agents by means of a ribbon mixer. This requires only a few minutes. The blended scrap-and-oil mixture is placed in shallow pans, which are in turn stacked on small flatcars on rails. Several of the flatcars can be pushed into the pressure vessel for simultaneous devulcanization of their charges. Depending on the size of the devulcanizer, 7,000 to 12,000 pounds may be reclaimed at one time. Live steam is admitted to the tightly sealed single-shell heater, and a pressure of 185 pounds per square inch is maintained for 5 to 6 hours. At the end of this period the pressure is released, and the pans of scrap are removed to the mill room for final working and compounding. The process is simple in operation; it has some advantages in that no losses of rubber particles are incurred and no washing or drying steps are required.

The Mill Room

Because of its tremendous power consumption and the large amounts of cooling water required, the mill room is by far the costliest in operation of all the departments of the reclaiming plant. If reclaim is to process well in the ultimate manufacture of rubber goods, it is essential that a great amount of mechanical work be expended on it during the final steps of the reclaiming operation.

The devulcanized rubber polymers coming from the dryers are transferred to an internal mixer (7E) where they are blended with fillers and plasticizers or any materials needed to impart specific characteristics. Batches of approximately 450 pounds can be handled in this way in only a few minutes. The fillers such as clay, carbon black, and whiting and the plasticizers such as asphaltic materials are standard compounding ingredients in general use in the rubber industry (20). The blending operation can also be carried out on a two-roll mill, having a roll length of 60 inches and roll diameters of 20 and 22 inches, respectively. The devulcanized dried stock is first massed together on the mill and then blended for 5 to 6 minutes with the various ingredients. The batch size is about one third that obtainable in the internal mixer, and the operation is slower.



Strainer Removes Any Remaining Foreign Particles Before Rubber Is Conveyed to Finishing Mills

A preliminary refining (breaking) follows the blending operation. The breaker is a two-roll mill with one roll 24 inches in diameter and the other 21 inches. At its rotational speed of 40 r.p.m., the larger roll has a peripheral speed of 254 feet per minute; the friction ratio of the rolls is high, about 2.5:1, and the quantities of cooling water required to remove the friction-generated heat are substantial. The mills exert a high pressure on the rubber stock during the mastication process, and the rolls are short (36 inches) to prevent distortion at the pressures developed. The rolls are smooth and accurately crowned, and the rubber is converted to a relatively homogeneous sheet approximately 0.015 inch thick.

This sheet is discharged into a pit containing a screw conveyer, which feeds it to a strainer (11E) for removal of any remaining foreign particles. Small bits of brass and other nonferrous materials, against which the magnetic separators are ineffective, are removed by this apparatus which resembles a huge meat grinder. The stock is forced along by a screw and is extruded through the openings of a 20-mesh screen backed by a heavy plate with perforations about 0.25 inch in diameter. The rubber leaves the backing plate as a mass of continuous, plastic rods; these are automatically sheared off at short intervals by rotating knives and conveyed to the finishing mills.

The refining or finishing mills are exactly like the preliminary refiners or breakers and are the last major processing equipment in the reclaim sequence. The rolls are set much closer together for the finishing operation, and the product is sheeted out to a thickness of only 0.004 to 0.006 inch. Cooling water is supplied to the refiner rolls at a rate sufficient to hold the surface temperature of the rolls at about 170° F. Any partially digested particles



East St. Louis, Ill., Plant of Midwest Rubber Reclaiming Co.

which are not sufficiently workable to pass through the narrow opening are gradually worked to the edges of the mill and periodically removed as "tailings." The small amounts of tailings, averaging about 3% of the total stock processed, are usually returned to the devulcanizers for a second digestion treatment.

The thin sheet produced by a finishing mill is allowed to build up on the water-cooled windup roll until a hollow cylinder with a wall thickness of about 1 inch is formed. This cylinder is then cut from the roll lengthwise, forming a slab of reclaim weighing about 30 pounds. The slabs are dusted with talc to prevent sticking and are then carefully stacked on pallets in a manner which allows air to circulate between slabs, releasing any heat which might still remain in the stock. Trucks remove the filled pallets to the warehouse where the reclaim is securely baled with steel bands. From the warehouse, the finished product can be loaded directly into boxcars or trucks for shipment.

Control and Development Laboratories

Purchasers of reclaim demand complete analyses of the stocks they use, and Midwest's factory control and development laboratories maintain a close check on composition and properties of the reclaim in process. The general appearance of the reclaim, specific gravity, and physical properties—such as tensile strength, modulus, elongation, and hardness—and processing properties are tested at specified intervals. For this purpose the reclaim is milled, compounded, and vulcanized, according to a simple test formula (Table I), and is tested under controlled humidity and temperature conditions in accordance with A.S.T.M. D-11 test procedures. This test is used by general agreement throughout the industry.

Chemical analyses, such as the determination of acetone and chloroform extracts, ash, carbon black, and cellulose content, alkalinity, and rubber hydrocarbon content by difference as well as by direct analysis are carried out regularly. The direct analysis, by chromic acid oxidation, reveals the amount of natural

rubber present in a mixed stock. Records of all these tests are kept, and each shipment can be traced to these records.

Aside from these routine tests, certain specific tests are conducted in correlation with the ultimate use of the reclaim in the manufacture of rubber goods. These tests are carried out by compounding the reclaim into formulations representative of those used in the rubber industry for the manufacture of tires, battery boxes, adhesives, automotive articles (steering wheels, radiator hose, weather and windshield stripping, gaskets, clutch and brake covers, bushings and mats) and mechanical goods such as garden hose, belting, household goods, baby carriage and toy tires, soles, and heels.

Special reclaims are produced to fit ultimate uses, and special equipment is required for testing them. For example, to test the suitability of a reclaim for the various uses in tire compounding—these constitute almost 50% of the total yearly consumption of reclaim—heat build-up is tested in a Goodrich flexometer. Flex resistance is tested in a De Mattio flexometer, and restored energy (elasticity) is calculated from the results obtained from a Goodyear Healy, or Lüpke rebound machine. Abrasion is measured by a Grasselli type abrasion machine as well as by the National Bureau of Standards type machine. Finally, to test the reclaim under actual running conditions, tires are built containing this reclaim, and their performance is compared with that of tires of the same compound formulation but

TABLE I. RECLAIM TEST FORMULA (34)

(Cure 10, 15, 20 minutes at 287° F.)

Ingredient	Parts
Reclaim (RHC)	200
Zinc oxide	10
Stearic acid	4
Sulfur	6
Mercaptobenzothiazole	1
Diphenylguanidine	0.4

without the reclaim under test. These tires are evaluated either on regular test fleets or on cab fleets in the vicinity of Midwest's factories. Tread inspections and nonskid measurements are made at regular intervals. Failures as differentiated from tread wear are also recorded, and the performance of each tire is closely observed in varying weather conditions.

In other fields of use the speed of extrusion, plasticity, rate of cure, impact strength, indentation resistance, resistance to ultraviolet light and to heat or oxygen aging may be determined.

To handle the compounding and vulcanization of the test samples, three laboratory mills with 6 × 12 inch rolls, one four-speed size B Banbury mixer, and two hydraulic steam heated presses are in continuous use. The mills and the Banbury are connected with a recording wattmeter so that the power requirements during mixing can be observed; these indicate the processing properties of the reclaim under consideration.

Finally, a small pilot plant, consisting of digesters, devulcanizers, and washing, drying, and refining equipment, is available for the testing of new reclaiming oils and catalysts.

Utilities and Auxiliary Equipment

Steam is a most important commodity in the reclaiming of rubber, and the East St. Louis plant is in a strong position in this regard. Two identical watertube boiler units, each with a capacity of 361 hp., were installed when the plant was built in 1928. Improvements effected since that time have boosted the capacities of the two units to 500 hp. each. Either boiler is capable of supplying the total requirements of the plant at current rates of consumption; the other is a stand-by unit for use during maintenance shutdowns of the operating unit or to allow for the possibility of future plant expansions. Steam is supplied to the plant at a pressure of about 190 pounds per square inch, and peak demands as high as 40,000 pounds per hour have been met by the single boiler, with a pressure loss of less than 5 pounds per square inch. One half pound of coal is consumed for each pound of reclaim produced.

Electric power demand at the East St. Louis plant is normally about 5000 kilowatts, purchased in toto from the Union Electric Co. Power is received at 13,800 volts, reduced to 2300 volts by Midwest's first bank of transformers, and to 440 volts by a second bank. Each pound of reclaim produced requires the expenditure of 0.6 kw.-hr. in electrical energy.

A major portion of the plant's power consumption is attributable to the tremendous synchronous motors (6E) which drive the banks of crackers, breaker mills, and refining mills (1E, 7E). Three crackers, or as many as eight breaker and refining mills are mounted on a single shaft, and the entire bank is driven by a single slow speed motor. These motors operate at 2300 volts with a rated horsepower of 300 to 1000 each. Twelve of these are in use in the plant.

Cooling water in great quantities is required to remove the heat generated during the blending, breaking, straining, and refining steps. Midwest has drilled its own wells, three in number, to ensure an adequate supply of water at relatively low temperatures. The wells are 110 feet deep and supply water to the plant at 60° F.

Other than the provision of steam, power, and water, the principal side issue in the rubber reclaiming plant is the problem of storage for the large volumes of liquid chemicals required. Both technical caustic and zinc chloride solutions are purchased in tank car quantities, at a concentration of 50%. In order to prevent solidification or settling at this concentration, the solutions must be warm: Midwest has solved this problem by storing these materials in a large tank house, maintained at about 90° F.

Underground tanks are supplied for all flammable materials, such as crude solvent naphtha. As in the case of the caustic and zinc chloride solutions, the reclaiming oils are purchased in tank

TABLE II. COMPOSITION AND PROPERTIES OF WHOLE-TIRE RECLAIM—1947-50

	1947	1948	1949	1950
Specific gravity	1.17	1.17	1.17	1.17
Acetone extract	15	17	17	17
Cured chloroform extract	1	1	1	1
Ash	11	10	10	10
Cellulose	Nil	Nil	Nil	Nil
Carbon black	19	18	18	18
Rubber hydrocarbon (by difference)	52	52	52	52
Rubber hydrocarbon (by direct analysis ^a)	38	33	33	34

^a Indicative of natural rubber content.

car lots. The storage tanks for the oils and solutions range in size from 4500 to 12,000 gallons each, and a total storage capacity of 130,500 gallons is available. Solid chemicals are stored in bags or drums in the warehouse.

PROPERTIES AND USES OF RECLAIMED RUBBER

Although reclaiming was originated for the specific purpose of providing a substitute for new rubber, technological evolution has allowed reclaim to emerge as a raw material in its own right, with many unique properties and with advantages over new rubber in several applications, such as adhesives. The extraordinary uniformity of the product is evident from the chemical analysis of a whole-tire reclaim over a period of years (Table II).

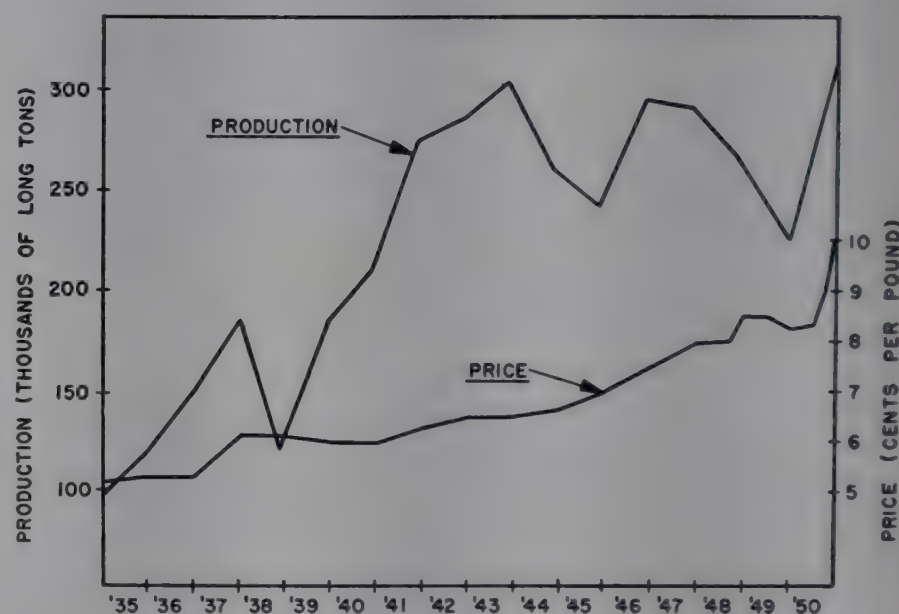


Figure 8. Production and Prices of Reclaimed Rubber—1935-50

In general, reclaim allows faster and easier mastication and mixing than new rubber, with attendant savings in time and power consumption during compounding. Neutral process reclaims, especially the newer ones containing GR-S, permit faster extrusion and calendering than either natural or synthetic new rubber, since they are less scorchy—that is, they are less susceptible to premature vulcanization by the heat developed in the extrusion and calendering processes (23, 29). As an additional advantage, control over dimensions during these processes is improved.

Because it is less thermoplastic than new rubber, reclaim helps molded or extruded articles to retain their shape during vulcanization or curing. Because it is less nervy, it is less susceptible to shrinkage in the uncured state. This is of particular importance in the manufacture of such rubber goods as automobile mats where calendering and vulcanizing conditions are such that shrinkage can occur.

Cements made from reclaim exhibit a comparatively low viscosity for high concentrations of solids, and the films obtained from reclaim cements possess a high modulus. These phenomena make reclaim indispensable in the manufacture of many

TABLE III. COMPARISON OF RECLAIM PRODUCTION AND CONSUMPTION WITH NEW RUBBER CONSUMPTION—1935-50 (33)

Year	Production of Reclaim ^a , Long Tons	Consumption of Reclaim ^a , Long Tons			New Rubber Consumption, Long Tons	Ratio, Total Reclaim to Total New Rubber
		Transportation items	Nontransportation items	Total		
1935	119,906	117,500	491,544	0.239
1936	150,571	141,500	575,000	0.246
1937	185,000	162,000	543,600	0.298
1938	122,400	120,800	437,031	0.276
1939	186,000	71,477	98,523	170,000	592,000	0.287
1940 ^b	208,971	73,280	116,920	190,244	651,060	0.292
1941 ^b	274,202	84,000	167,231	251,231	781,259	0.322
1942	285,114	90,736	164,084	254,820	394,442	0.647
1943	303,991	118,792	172,290	291,082	488,525	0.595
1944	260,607	76,875	174,208	251,083	710,783	0.353
1945	243,309	96,798	144,238	241,036	799,009	0.302
1946	295,612	107,930	167,480	275,410	1,039,296	0.265
1947	291,395	116,581	171,814	288,395	1,122,207	0.259
1948	266,861	112,408	148,705	261,113	1,069,404	0.244
1949	224,029	111,038	111,641	222,679	988,903	0.226
1950 ^c	310,000	144,000	159,000	303,000	1,240,000	0.244

^a Reported to U. S. Dept. of Commerce by producers or consumers of reclaim.

^b Official estimates, U. S. Dept. of Commerce.

^c Unofficial estimates based on U. S. Dept. of Commerce figures, January-October 1950.

used, in spite of the fact that first-line tire reclaim was selling for over 4 cents per pound.

During the last 15 years, prices of reclaimed rubber have shown a gradual upward trend (Figure 8), but they have been much more stable than the prices of natural rubber. The price of reclaim, in fact, has long served as a stabilizer for the price of new rubber.

Production costs at Midwest during periods of capacity operation may be broken down approximately as follows:

To suppliers, for scrap rubber, manufacturing supplies, and services	55%
To employees for wages, salaries, and employee benefits	40%
Depreciation and amortization	5%
	100%

industrial adhesives. Because reclaim is capable of taking up high filler loadings in a very short time, because its rate of cure is high, and again because it does not scorch easily, its use is advantageous in the manufacture of hard rubber goods such as battery cases.

While the fundamental properties of reclaim will reflect the properties of the kind of elastomer hydrocarbon it contains, its principal advantage, perhaps, lies in its adaptability. Since it is a manufactured raw material, it can be modified during manufacture to meet individual specifications, becoming a tailor-made raw material for the user with a specific production problem.

U. S. Department of Commerce figures (Table III) show that approximately half of all reclaim produced in the United States now goes into transportation items, consisting of tires, tubes, and tire repair materials (33). In general, reclaim is not used to any large extent in the tread of the tire. However, a tread compound made from cold rubber and reclaim will outwear a tread compound containing natural rubber only (26). In tire production practice, the use of reclaim is not limited to any specific grade of tires.

Many other items of automotive equipment, such as battery boxes, floor mats, radiator hose, and window channeling, all classified by the U. S. Department of Commerce as nontransportation items, are volume consumers of various types of reclaim; automobiles, therefore, utilize an estimated two thirds of all reclaim produced (2). A first-quality tire for passenger car use normally contains from 3 to 4 pounds of reclaim; an automobile floor mat may contain 5 pounds and a battery case an equal amount. The principal uses of reclaim aside from those in the automotive field are in the manufacture of adhesives and mechanical and molded goods. Properly used, reclaim is not introduced where any impairment of quality of the finished product will result. In some products it gives better quality than can be obtained with new rubber, and its use often results in an equal quality at lower cost.

ECONOMICS AND PRODUCTION COSTS

Reclaim is no longer considered primarily a substitute for crude elastomers, but it does find increased markets during periods when crudes are available only in limited quantities or at very high prices. When crude rubber prices are unusually low, the reclaiming industry is certain to feel severe price competition, especially from off-grades of natural rubber. Even at such times, however, reclaim is required for many uses because of its special properties, and demand remains substantial (32). In 1932, when the price of crude rubber averaged only 3.4 cents per pound, reclaim still accounted for nearly 19% of all rubber

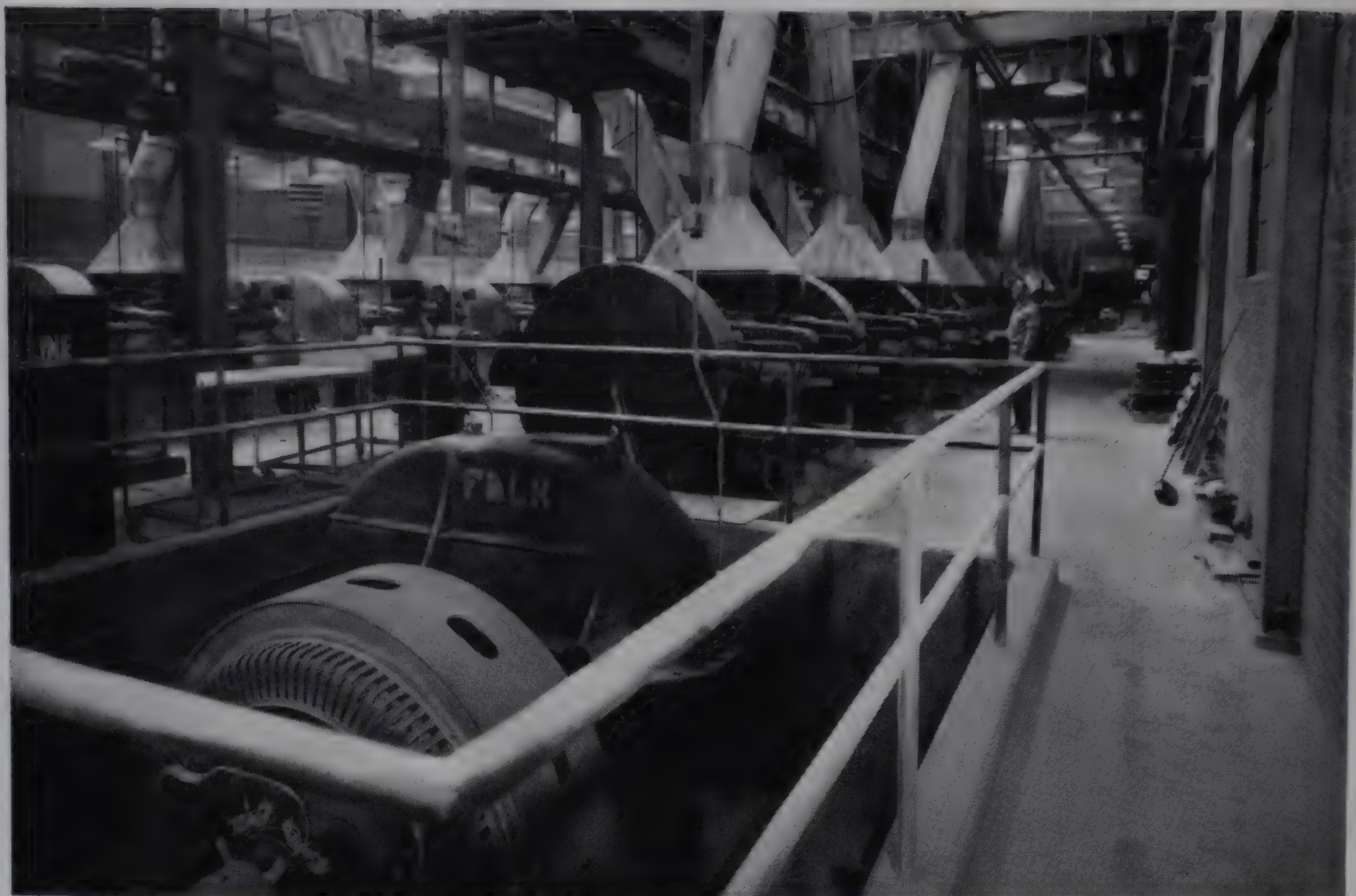
These production costs account for 80% of the sales dollar; the remainder is divided among taxes, dividends to stockholders, and earned surplus retained for use in the business. The interrelationship of these cost factors is sensitive to production volume, and operation at levels below capacity causes an increase in the ratio of wages and depreciation costs to total sales.

FUTURE PROSPECTS

In the latter half of 1950, the combined effects of high prices of natural rubber, government restrictions on its use, and the physical shortage of available new rubber caused a large increase in demand for reclaim. Production was immediately stepped up throughout the reclaiming industry, and predictions for 1951 production of as much as 350,000 long tons have been announced. This would exceed by a considerable margin the peak wartime rate of 304,000 long tons established in 1943. The capacity of the reclaiming industry has been increased considerably since the end of World War II, but a period of maximum effort appears to be ahead for all reclaimers.

It is unquestionably true that synthetic rubber polymers are here to stay. Inasmuch as research for new and better-performing synthetic rubber polymers can be expected to continue at full speed, new polymers will continually be developed. Some will reach production on a large scale. If these polymers are to be reclaimed successfully, either singly or in combination, the reclaimers must attain familiarity with their structure and chemical make-up and find the proper reclaiming agents. Usually there is a lag of 1 to 2 years between the first major production of these polymers and their arrival at the reclaiming factory; research can make effective use of this time.

There are, of course, still considerable improvements to be made in the mechanical equipment and its efficient use; a well controlled continuous process is the desirable goal. To justify replacement of the long-established digester process, any new development must offer exceptional advantages either in cost of operation (including equipment maintenance and replacement), in percentage of tailings produced, or in physical properties of the reclaim produced. The relatively low level of the price of reclaim and the stability of this price place severe restrictions on the introduction of new processes. Any economical substitution of processes, continuous or otherwise, or any improvement in the physical properties of reclaim, preferably combined with a decrease in manufacturing cost, would constitute a major contribution since it would permit greater advantages in the use of reclaim even at a time when crude rubber hydrocarbons might be available at a low price.



View of Mill Room Showing Synchronous Motor and Speed Reducer for Operation of Mills on Common Shaft

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- (2E) Anderson, V. D., Co., Cleveland, Ohio, screw-type expellers.
- (3E) Buffalo Foundry & Machine Co., Division of Blaw-Knox Co., Buffalo, N. Y., drum dryer.
- (4E) Builders-Providence, Inc., Providence, R. I., Toledo-Chronoflo automatic conveyer scale, Type 9153.
- (5E) Dorr Co., New York, N. Y., mechanical thickener.
- (6E) Electric Machinery Manufacturing Co., Minneapolis, Minn., 2300-volt, slow speed synchronous motors.
- (7E) Farrel-Birmingham Co., Inc., Ansonia, Conn., No. 11 Banbury mixer, Size B Banbury mixer, two-roll mills.
- (8E) Louisville Drying Machine Co., Louisville, Ky., dewatering presses.
- (9E) Oliver-United Filters, Inc., New York, N. Y., vacuum drum filter.
- (10E) Orville-Simpson, Cincinnati, Ohio, Rotex screens.
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